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A SCHOOL CHEMISTRY

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HEAD SCIENCE MASTER, MILITARY AND CIVIL SIDE
CHELTENHAM COLLEGE

OXFORD

AT THE CLARENDON PRESS

LONDON EDINBURGH GLASGOW NEW YORK

TORONTO MELBOURNE BOMBAY

HUMPHREY MILFORD

1917

19.346 478.

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PREFACE

THIS book appears as the result of a demand for a somewhat shorter course of School Chemistry than the authors' *Elementary Chemistry: Progressive Lessons in Experiment and Theory*.

The general method of treatment remains the same as the earlier work, viz. :—

(a) Clear directions are given for practical work, to liberate the teacher from explaining details of manipulation.

(b) Questions follow each experiment, to focus attention and ensure reflection.

(c) Frequent problems are inserted, to exercise the power of application of quicker pupils, and to keep the members of a given class fairly well together.

(d) Theory is developed *pari passu* with experiment.

The first five chapters deal with the preliminaries of manipulation, including practice in simple quantitative work.

Chaps. VI–IX, a study of combustion in air, present a type of the general method of chemical investigation suitable for beginners.

Chaps. X–XIII deal with classification of materials, the nature of oxides, water, and acids, leading up to the constitution of salts.

Equivalent weights and the atomic theory are then introduced, and are followed by a study of the chief non-metals and their compounds, together with a few typical metals.

Although not written to meet the requirements of any particular examining body, the book will be found to contain

PREFACE

the subject-matter common to many examinations, e.g. the Army Entrance Examinations; the Matriculation Examination of the Universities of London, Birmingham, and Wales, the Northern Universities; the Oxford and Cambridge Locals, &c.

Experience has shown that if the answers to the questions on each experiment are looked over and corrected *in the laboratory*, only a cursory inspection of fair note-books is required to ensure neatness and adequacy of description. This method greatly saves the time of the teacher.

The authors take this opportunity of thanking their colleagues and others for suggestions; they will welcome any further suggestions and criticisms from teachers at any time.

F. R. L. W.

G. W. H.

September, 1911.

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CHAPTER I

CONSTRUCTION OF SIMPLE APPARATUS

The following instructions for taking and writing out notes on experiments should be carefully read before practical work is begun.

Rules for writing notes.

It is advisable to employ two notebooks, one for use in the laboratory and a fair notebook for a more permanent and complete record of the work.

The Laboratory Notebook should contain all the subjects mentioned under the heading **LABORATORY RECORD**, placed at the end of most experiments. Arrange thus:—

- (1) The **number** and **title** of the experiment.
- (2) A record of all **observations**,* **weighings**, and **measurements**.
- (3) A **diagram** of the apparatus used.
- (4) **Answers to the questions**.

The Fair Notebook should contain a *full account* of the work. *It is very important that the description should be clearly expressed in good English.* Arrange thus:—

- (i) The **number** and **title** of the experiment.
- (ii) A **description**, in your own words and in the first person, *of what you actually did*. (Refer to the 'Directions' for guidance, but do not copy them *verbatim*.) Include the **observations**, &c. from Lab. Notebook. Draw **diagrams** on the opposite page.
- (iii) A list of **conclusions** drawn from the experiment. (Compose these from the corrected answers to the questions on the experiment, so that they may be understood without further reference to the questions.)

* These are usually distinguished by the word '**note**' or '**record**' in the directions.

Exp. I. Examination of a Bunsen burner.

Required:—(Exp. 1 and 2) Bunsen and bat's-wing burners, asbestos thread, scrap glass tubes.

DIRECTIONS. *A.* Notice the holes for admission of air near the base. Unscrew the tube, and notice the holes for the issue of the coal-gas. Then light the gas. **Note** the shape and colour of the flame.

Turn off the tap, replace the tube, *closing* the holes at the base, and relight. **Note** the different shape of the flame. Also **note** whether the flame is equally luminous all over or not, e.g. (*a*) just above the tube, (*b*) at the edges, (*c*) middle, (*d*) top.

Hold a glass tube in the flame. **Note** the deposit.

Open the holes at the base and hold the tube just used across the middle of the non-luminous* or blue flame, and observe what happens to the black deposit.

B. Hold some asbestos thread horizontally across the non-luminous flame, starting at the bottom.

Note where it gets hot first.

Raise it gradually to higher parts of the flame. **Note** each result.

C. Repeat *B* using the luminous flame.

LABORATORY RECORD.† Observations made in *A*, *B*, and *C*. Diagram to show structure of (*a*) the burner, (*b*) the non-luminous flame.

Questions:—(i) Which flame is longest, the luminous or the non-luminous?

(ii) Which are the hottest parts of the luminous flame?

(iii) Which kind of flame is hottest? (If in doubt, try which will melt a thin glass fibre quickest.)

(iv) Which flame would you use to heat a flask and why?

* The non-luminous flame is called the 'Bunsen flame'.

† The title **LABORATORY RECORD** is to show what must be recorded in your Laboratory Notebook, in addition to the number and full title of the experiment. Answers to the questions are to be included, and the whole should be submitted for inspection before proceeding to the next experiment.

Exp. 2. Examination of a bat's-wing burner.

DIRECTIONS. Notice the holes from which the gas issues, then light the burner. **Note** the colour and shape of the flame.

Test for the hot and cool parts with asbestos thread.

Draw a **diagram** showing the luminous and non-luminous parts of the flame.

LABORATORY RECORD. Observations and diagrams.

Questions:—(i) In what way does the shape of the flame differ from that of a Bunsen burner?

(ii) In what ways is it less suitable for heating a flask of water than an ordinary Bunsen flame?

Required for Exps. 3-II:—Triangular and rat-tail files, scrap glass tubes of various widths, glass rod, luminous bat's-wing burner.

Exp. 3. To divide narrow glass tubes.

Lay the tube † on the bench, make a scratch with a triangular file at the point at which it is desired to cut it.

Hold the tube in both hands, placing the thumbs on the side of the tube opposite to the scratch.

Press the thumbs against the tube, and pull the ends of the tube towards you.*

Exp. 4. To break off a jagged end.

Make a scratch as before, and place the tube †, with the scratch uppermost, on the edge of a file lying on the bench. (The edge of the file must be vertically below the scratch.)

Hold the tube firmly in position, and knock off the jagged end with a key or other heavy object.

Draw a **diagram** to illustrate the operation.*

* The tubes used in Experiments 3-9 should, when finished, be submitted for inspection along with the laboratory notebook.

† Short pieces of scrap tubes should be used, if available.

Exp. 5. To divide wide glass tubes.

A. If the tube has thin walls, make a sharp scratch as before; now take a piece of glass rod and heat the end in the Bunsen flame. When it is soft, flatten it by pressing first one side and then the other on the foot of the burner. Heat the flattened end till red hot, press the edge along the scratch so as to start a crack which can be made to follow round the tube. Practise this until you can do it well.*

B. If the tube has thick walls, make a scratch completely round it. If it cannot be broken by gentle pressure of the hands, use a hot glass rod as before.

Exp. 6. To round the edges of a glass tube.

Before glass tubes are used for any purpose, the sharp edges must be rounded by being heated near the top of a Bunsen flame.

A. Hold the tube nearly vertically in the flame and keep it revolving on its axis until the edges are red hot.*

Precaution :—Avoid heating the tube too long. Find out the reason for this precaution, by keeping another tube in the flame for a longer time.

Note the difference in the width of the bore of the two tubes at their ends.

B. Cut off two pieces of glass rod 2 dm. long, round the edges, and keep for subsequent use as 'stirring rods'.

Exp. 7. To draw out a narrow tube from a wide one.

Hold the tube* across the *Bunsen flame* near the top.

Keep it rotating until it is red hot, and *quite soft*.

Then take it out of the flame and draw the ends apart carefully till the tube is of the required diameter.

A tube of very narrow bore is called a '*capillary tube*', from the Latin *capilla*, a hair.

* Short pieces of scrap tube should be used.

Exp. 8. To seal a glass tube.

Hold a piece of fairly wide (1 cm. diam.) tube* in both hands across, and near the top of a *Bunsen flame*.

Rotate it constantly until it is quite soft.

Take it out of the flame, and while still rotating it, pull gently at the two ends.

Allow it to cool, and cut the tube at the narrow part.

Close up the end by melting, heating it strongly.

Take it out of the flame, and blow gently down the tube so as to press out the end to the same width as the rest.

Exp. 9. To blow a bulb on a tube.

A. At the end. Heat the end of the tube sealed in Exp. 8 and *gently* blow it out forming a *very small* bulb. Now heat the glass above this bulb in a Bunsen flame,† and as it softens rotate the tube on its axis. When thoroughly soft, withdraw from the flame and while still rotating blow gently into the tube. Practise until a good spherical bulb of even thickness is produced.

B. At the middle. Cork one end of a piece of straight tube and heat it in the middle rotating it continuously. When it softens press inwards from each end so as to provide enough glass for the bulb. Withdraw from the flame, hold it horizontally and blow gently revolving it all the time.

Submit your results for inspection.

LABORATORY RECORD.

Brief description and diagrams for Experiments 3-9.

[For Fair Notes write a *full* description in your own words and lay stress on the precautions necessary for success. Great care should be taken with the description and good diagrams should be drawn, see p. 1.]

* Use short pieces of scrap tubing.

† If the glass is hard a blow-pipe flame should be used.

Exp. 10. To bend glass tubes.

In order to bend a tube, so that the bore may remain of uniform thickness, it must be *evenly heated all round*.

DIRECTIONS.—*A*. Hold a piece of narrow tubing horizontally with both hands in a Bunsen flame. Rotate it until soft.

Take it out of the flame and bend it at right angles.

Note whether the bore of the tube is altered at the bend.

B. Repeat *A*, bending the tube in the flame.

Note whether the result is better or worse.

C. Repeat *A* and *B*, using a **luminous bat's-wing burner** with a flame about 5 cm. wide.

Hold the tube horizontally *along* the flame, not across it.

When it is quite cold wipe off the soot.

D. Having found which flame is best, use it to make a right-angled bend, with one limb 8 cm. long, and the other 18 cm. Use a straight tube not less than 30 cm. long. Make the side last in the flame form the concave part of the bend. Round the edges, and keep for future use.

LABORATORY RECORD. Diagrams of the bends *A*, *B*, *C*.

Questions:—(i) Which flame is best for bending a tube and why?

(ii) Why must the tube be rotated before bending it?

(iii) Draw a large diagram of each of the bent tubes.

(iv) Is it best to bend the tube inside, or outside the flame? Explain why.

(v) What is the effect on the bend of the glass getting too soft? (If in doubt, try it.)

Submit your bent tubes for inspection.

Exp. II. To bend a tube at given angles.

A. Draw two lines AC and BC on paper, meeting at C at an angle of 35° .

Rotate a tube (3 dm. long) in a luminous *bat's-wing flame* till soft, so that the heated part is about 1 dm. from one end.

Take it out of the flame, and hold it so that the middle of the hot part is just over C . Bend the tube until the two limbs coincide with CA and CB .

Cut off the limbs down to 8 cm. and 18 cm. respectively.

Fig. 1 represents the properly bent tube.

B. Bend two tubes at an angle of 120° , so that the limbs of the first are 10 cm. long, and of the second 32 cm. and 2 cm. respectively. Use the same method as in A.

The first bent tube should appear as in Fig. 2.

C. Bend a tube (40 cm. long) twice at right angles, having the ends of the tube pointing the same way.

The lengths of limbs are shown in Fig. 3.

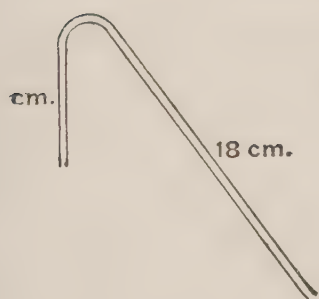


FIG. 1.

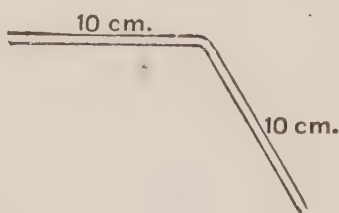


FIG. 2.

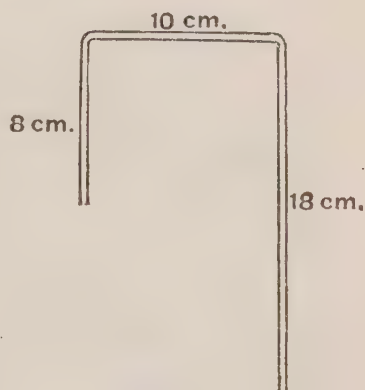


FIG. 3.

Precaution :—Be careful that the limbs are in the same plane, so that the bent tube will lie flat on the bench. Repeat the experiments, if not successful at first.

Round the edges, and keep these tubes for future use.

Submit the bent tubes for inspection.

Exp. 12. To bore a cork.

Required:—Corks, cork-borers, rat-tail file.

The object of boring a cork is usually to enable a glass tube to be pushed through it, so that it fits perfectly tight.

You may take a cork and try to bore a hole with a borer in your own way. If unsuccessful, try again, carrying out the following *directions*:—

- (a) Take a glass tube which is to pass through the cork, and press the end on the narrower end of the cork, so as to form a circle on the cork.
- (b) Choose a borer slightly narrower than the glass tube. See that the borer is sharp. (If not, *gently* file the edges.)
- (c) Place a cross piece through the hole at the top of the borer so as to form a handle.
- (d) Hold the cork with its broader end in your left hand and bore the hole by turning the borer like a corkscrew, half a turn at a time.

Moisten the glass tube (the edge being rounded) and carefully push it through the cork.

Unless it fits tightly another cork must be bored.

If it is too tight to pass through gently, file the cork *evenly* with a rat-tailed file.

Submit the bored cork for inspection.

NOTE.—In choosing corks for flasks be careful to see that they will fit tightly and are not too hard. A cork which is rather too large or too hard may be made to fit by *gently* rolling it under a book, or by *gently* squeezing it in a cork-presser.

Since corks are not perfectly conical and the necks of flasks are not perfectly cylindrical, a leak may often occur if the cork is too hard. It should be softened, so that when pressed into the neck of the flask it will naturally bulge out to fill up any space which would otherwise remain between the cork and the glass.

Exp. 13. To fit up a wash-bottle.

Required:—Flask (about 500 c.c.), cork, glass tubes.

DIRECTIONS. Apply what you have learnt by fitting up a wash-bottle as shown in Fig. 4.

When made, test to find whether it is air-tight or not by stopping up one tube with a finger and sucking up the other tube. If air can be sucked through there is a leak. Find out where it is and remedy the defect by boring another cork if necessary.

N.B. It is most important to test a piece of apparatus for leaks as soon as it is made, otherwise much time will be wasted. Never use grease or vaseline to stop a leak—bore another cork.

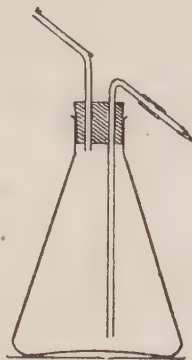


FIG. 4.

Submit the apparatus for inspection and then rinse out with distilled water; fill it with distilled water and keep for future use.

Exp. 14. To dry a wet flask quickly.

Required:—Small flask, glass tube, foot-bellows.

DIRECTIONS. Wash out a flask with water and dry it on the outside; pass a glass tube into the flask, so that a blast of air can be blown through it, either from the mouth or by attaching it to the rubber tubing from the foot-bellows.

Hold the flask mouth downwards on the tube at some distance above a Bunsen flame of medium size; rotate the flask slowly, and blow a stream of air into it until it is quite dry.

Any moisture which remains in the neck of the flask may be removed by means of blotting-paper.

Hints on fitting up apparatus.

1. Before bending tubes be sure that you know the angle and the length of the limbs required. Always make the latter a little longer than is necessary and cut them down.
2. Bore corks a little narrower, if anything, than is required, and widen the hole with a round file if necessary.
3. If a tube or thermometer has to be pushed through a cork, moisten it with water and push gently with a cork-screw motion. If too much pressure is applied it is liable to break and cut your hand.
4. See that the apparatus is air-tight and clean before beginning to use it.
5. When the apparatus is to be fixed on a stand, see that the whole is **neat** and **convenient for use**, and in a position where it is not likely to be knocked over.
6. Never heat flasks over an open flame, but place wire gauze or some form of heat distributor underneath.
7. Remember that flasks, beakers, &c., are made of thin glass, and will easily break unless care is taken.
8. A rubber-tube connexion may be tightened by turning back the ends of the rubber over itself.
9. If a glass tube has to be fitted into a vessel with a *very narrow neck*, a piece of rubber tubing placed over the glass tube is often better than a cork.

QUESTIONS ON CHAPTER I.

N.B.—*Great care should be taken with the composition of the answers to these questions. They should be expressed in your own words, clearly and fully, so that a beginner after reading them would be able to perform the experiments without asking for more information. This is not easy to do without thought. Draw diagrams to illustrate your answers.*

1. Describe how (a) narrow, (b) wide glass tubes may be divided.
2. How are the edges of a glass tube rounded? What pre-

cautions must be taken, and why? What kind of flame is used? What is the object of rounding the edges?

3. Describe the process of sealing a glass tube at one end. Why is it important not to pull the ends very far apart after heating?

4. Draw a diagram of a Bunsen burner, and describe it fully.

5. Make a sketch of a bat's-wing burner, and explain why such a burner with a luminous flame is used for bending tubes. Draw a bend made with (a) a bat's-wing burner, (b) a Bunsen burner.

6. Why is it necessary to rotate a tube when it is being heated previous to bending? Why is the tube bent outside the flame and not in it? Describe how to bend a tube as in Fig. 3.

7. What is a capillary tube, and how is it made?

8. Describe how to blow a spherical bulb at the end of a glass tube, and state what precautions should be taken to avoid failure.

9. How is a bulb blown in the middle of a tube?

10. Describe fully how you bore a cork with a hole through which a glass tube can be passed so as to fit tightly.

11. In a flask fitted up as in Exp. 13 indicate where leaks may occur, how they may be detected, and how avoided.

12. Give an account of a way of drying a wet flask rapidly.

CHAPTER II

MEASUREMENT OF MASS AND VOLUME

Metric Tables.

VOLUME.

1000 cubic millimetres = 1 cubic centimetre (c.c.)

1000 cubic centimetres = 1 cubic decimetre (= 1 litre)

1000 cubic decimetres = 1 cubic metre (cu. m.).

The cubic centimetre (c.c.) and litre (l.) are the most often used in Chemistry.

The mass of 1 c.c. of pure water at 4° C. is one gram.

This is the fundamental unit of mass on the metric system.

MASS.

1 milligram (mg.) = 0.001 g.

10 milligrams = 1 centigram (cg.) = 0.01 g.

10 centigrams = 1 decigram (dg.) = 0.1 g.

10 decigrams = 1 gram (g.)

10 grams = 1 dekagram (Dg.) = 10 g.

10 dekagrams = 1 hectogram (Hg.) = 100 g.

10 hectograms = 1 kilogram (Kg.) = 1000 g.

Exp. 1. Examination of a box of weights.

DIRECTIONS. *A.* Look carefully at the weights and see how they are arranged and marked. Notice there are two kinds: the heavier ones of brass, and the lighter ones, usually of aluminium, or German silver.

Precaution:—Never touch the weights with your fingers, which would tarnish them; *always* use the forceps.

B. Write down the weights of each brass piece in your notebook and add up the total.

GRAMS	MILLIGRAMS
·5	500
·2	200
·1	100
·1	100
etc	etc
Total g	mq

FIG. 5.

Draw an oblong diagram, as in Fig. 5, and divide it into as many divisions as there are white metal weights.

In one column put down the values of the weights as decimals of a gram; in the other give their corresponding values in milligrams.

Add up both of them, and put their totals at the end.

What is the sum of *all* the weights in the box?

N.B.—The white metal weights are marked by some makers in milligrams, and by others in decimals of a gram, and sometimes in all the three subdivisions of a gram. See that you thoroughly understand the markings on the pieces in your particular box.*

* It is desirable for beginners always to use the same box of weights until they are familiar with it. It is therefore useful to have the boxes numbered.

Exp. 2. To illustrate the principle of the balance.

Required:—As in Fig. 6 and box of weights.

DIRECTIONS. *A.* Put a triangular block of wood on the bench, and balance a half-metre, rule with its scale uppermost, on the edge of the block.

Note the point of support (F , Fig. 6) on the rule, so as to replace it quickly if it slips.

Place a 5-gram weight at each end of the rule and see whether they balance one another; if not, move one slightly until they do so.

Note the distance in millimetres between the middle of each weight and the point of support of the rule.

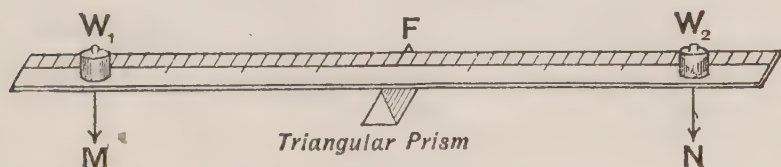


FIG. 6.

B. Find out where a 10-gram weight must be placed to balance 5 grams at the end of the rule, taking care not to alter the position of the rule on the block.

C. Repeat *B*, using 20 grams instead of 10 grams.

Find out for each of these cases whether the weight of W_1 multiplied by its distance from F = the weight of W_2 multiplied by its distance from F .

LABORATORY RECORD. Diagram and numerical results.

Questions:—(i) If in Fig. 6 W_1 is 3 grams, MF 20 cm., and W_2 5 grams, calculate the distance NF when the weights balance.

(ii) If W_1 is 7 grams, NF 15 cm., MF 20 cm., calculate the weight of W_2 when the weights balance.

Exp. 3. To examine an actual balance.

Required :—Balance, paper, box of weights.

DIRECTIONS. Put a clean piece of paper on the bench.

Take off the pans, and lay them on the right- and left-hand sides of the paper.

Lift the wire pan-holders from the stirrups which support them and put them by their pans.

Take off the stirrups and put them in their proper pans.

Now take hold of the knob at the centre of the beam, lift the beam from its support and lay it on the middle of the paper.

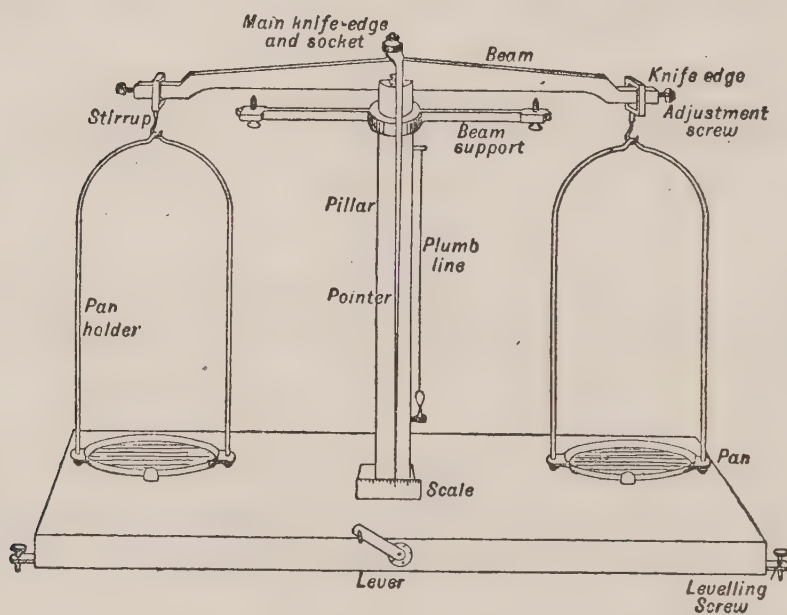


FIG. 7.

Examine, draw, and name each part of the balance.

Note the position of the knife-edges, and the planes on which they work, also the material of which they are made. [In good balances these parts are usually of agate, a very hard stone, which does not rust like steel, but is easily chipped by careless use.]

Move the lever which works in the base board backwards and forwards, and note the effect.

Replace the parts in their proper positions.

ADJUSTMENTS. (1) The plumb-line is to show whether the pillar is vertical. If necessary, turn the levelling screws until the point of the 'plumb' is just over the point fixed on the pillar.

(2) Turn the lever to the right, and set the beam swinging by gently fanning one pan with your hand.

Note whether the pointer moves over an equal number of divisions on the right and left of the middle mark on the scale. If it does not, turn the lever to the left, adjust the beam by screwing the nut at one end inwards or outwards as required, and try it again until correct.

Precaution :—*When adjusting the balance, and when adding or removing objects from the pans, the beam must always be at rest, i. e. the lever must be turned to the left.*

THE USE OF THE BRASS KNOB ON THE BEAM. Carefully unscrew and remove the brass knob.

With the aid of the forceps place a one-gram weight in each pan. Set the beam swinging so as to be sure that the weights balance one another.

Add 0.01 gram to the right-hand pan, and again set it swinging. **Note** whether the pointer indicates any difference in weight; if not, continue to add small weights until a difference is shown.

Replace the knob, and remove the decimal weights.

Now find the smallest additional weight which affects the swing of the pointer when the knob is in position.

The knob therefore increases the *sensitiveness* of the balance.

Rules for Weighing.

(i) *Adjustments.*

- (a) Adjust the levelling screws till the pillar is vertical.
- (b) See that the stirrups rest properly on their knife-edges, and that the main knife-edge is in the socket.
- (c) Set the beam swinging, and note whether the pointer swings over the same number of scale divisions on each side of the central line. If not, alter the nut at the end of the beam. [If the balance has a case, set the beam swinging and close the case to avoid disturbance by draughts.]

(ii) *The object to be weighed.*

- (a) See that it is clean, dry, and cold.
- (b) Take care that the beam is at rest when putting on or removing an object and weights from the pans.
- (c) Place it on the **left-hand** pan and the weights on the **right**. First try a weight which you think is a little heavier than the object; remove it if too heavy, and try smaller ones in order.

(iii) *The weights.*

- (a) Transfer them with forceps, not with your fingers.
- (b) Arrange them on the pan right side up and right way round, so that the figures are easily read.
- (c) Count them up on the pan,* and write down the total at once. *Check this result* by noting those absent from the box.
- (d) Return them to the box, beginning with the largest.

* Many mistakes are made by miscounting the weights. Besides being careful to arrange them tidily, it is useful to make a habit of always placing the decigrams in one row and the centigrams in another.

Exp. 4. Practice in weighing.

Required:—Numbered objects of known weight.

DIRECTIONS. Carefully weigh the following objects:—

A. The given wooden block. Record its number.

B. The given metal cylinder. Record its number.

Count up the weights when properly arranged on the pan, and *record* the total *at once*. Then check the result by counting the vacancies in the box.

The Rider. The principle illustrated in Fig. 6 is used for finding differences of weight less than a centigram.

The right-hand side of the beam of the balance, between the central and end knife-edges, is divided into ten equal

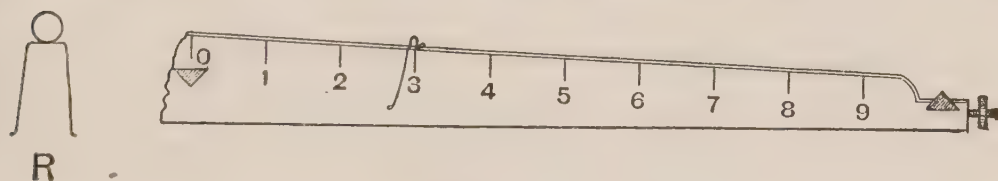


FIG. 8.

parts in the manner shown in Fig. 8. A piece of platinum or aluminium wire, weighing a centigram, is bent into the form shown at *R* in Fig. 8; this is called a rider.

If the centigram rider is suspended exactly over the end knife-edge it has the same effect as if it is placed in the pan on the same side, and it will balance an object weighing 1 cg. in the other pan. If, however, the rider is placed at any other point on the divided arm of the beam its effect is less than 1 cg. placed in the pan, and depends on its distance from the central knife-edge.

Thus, if the rider is hung at the eighth division it will counterpoise 0.8 cg. in the left-hand pan, at the fifth division 0.5 cg., at the third 0.3 cg., and so on.

It is therefore possible, by using a centigram rider and having the beam on one side divided into ten parts, to find differences of weight of 0.1 cg., i.e. 0.1 mg. or 0.001 g.

In very delicate balances the beam is often divided into 100 equal parts, and with such a balance and using a centigram rider it is possible to find differences of weight of 0.01 cg., i.e. 0.1 mg. or 0.0001 g.

The method of using the rider is as follows:—

The object to be weighed is put in the left-hand pan, and weights are put in the other until the addition of 1 cg. is found to be too much. The beam is brought to rest and the door of the balance is closed to exclude draughts.

The rider is now put on the beam by means of the carrier, and the latter having been raised, the beam is set swinging. If the pointer shows that the object is not counterpoised by the weights and the rider, the latter is moved until a position is found at which the two sides of the balance are exactly counterpoised.

C. Reweigh the wooden block and cylinder, using the rider.

LABORATORY RECORD. Record of weighings. [In the Fair Notebook write a *full* description of the method of weighing and of recording the results.]

Questions:—(i) How would it be possible to estimate the weight of an object to 0.01 cg., i.e. to 0.0001 g., using the centigram rider with the beam divided in tenths?

(ii) What advantage is gained by the use of the rider?

Instruments for measuring volumes. The volumes of an irregular solid lump, powders, and liquids, are best measured by the use of one of the vessels mentioned below. As these will frequently be used in later work, it is important that the methods of using them *accurately* should be thoroughly learnt.

Exp. 5. To use a graduated jar.

Required:—The jar, cardboard, black paper, gum.

DIRECTIONS. *A.* Examine the jar, and **note**:—(a) the unit of volume on which the graduations are based ;

(b) the volume between two successive scale *numbers* ;

(c) the volume between two consecutive *lines* on the scale.

B. Pour in some water, and **note** whether the surface of the liquid is—(a) straight or curved ; (b) one definite line or not.

Read off the volume of water from the scale, having the eye—(c) above, (d) below, (e) on the water-level.

Record each reading.

Hold the jar in your hand and read the volume again, keeping the eye level with the water.

Note the reading, and compare with (e).

Cut out a small rectangle of cardboard about 8 cm. \times 4 cm.

Paste a rectangular piece of black paper (8 cm. \times 2 cm.) on to it, so as to cover half the card. Place it behind the measuring jar so that the lower edge of the black paper is about 2 mm. below the level of the water.

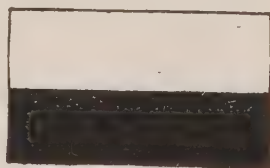


FIG. 9.

Note whether this makes the surface of the liquid easier to see or not.

Take another reading and compare it with (e).

Fill the jar up with water so that the reading is exactly 53 c.c. Use a glass tube to make the final adjustments.*

Submit the result for inspection. [Over.

* N.B.—A common mistake in reading scales to the nearest unit results from following the numbers with the eye from the wrong end of the scale. The eye should always follow the scale from the *zero end*, e.g. in Fig. 12 the reading is 10.8 *not* 11.2.

LABORATORY RECORD. Diagrams showing features noted in *A* and appearance of surface of water when seen against the card (*e*).

[In your Fair Notes also give a *full* and *careful* description.]

Questions :—(i) Which position of the eye in reading the graduations do you think is best, and why?

(ii) Why should the jar *not* be held in the hand while reading the level?

(iii) If the jar *holds* exactly 100 c.c. of liquid, on emptying it into another vessel would 100 c.c. be transferred or not?

Notes on the use of measuring vessels. The observations of the surface of the water in Exp. 5 will have shown that it

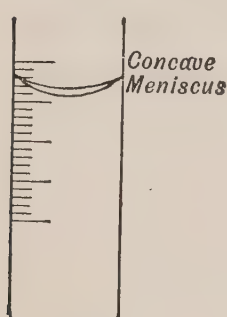


FIG. 10.

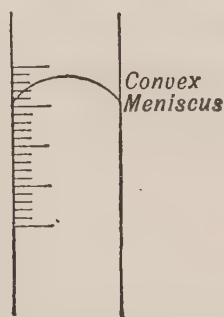


FIG. 11.

is not flat, but curved. Further, when you placed the card behind the jar you will have noticed two curves, one below the other. Such a curved surface is called a **meniscus** (crescent). When the liquid wets the vessel, as water does, the meniscus is concave (Fig. 10); but with those which do not wet the vessel, e.g. mercury, the meniscus is convex (Fig. 11).

With a concave meniscus the position of the lowest point against the scale must be taken as the reading.

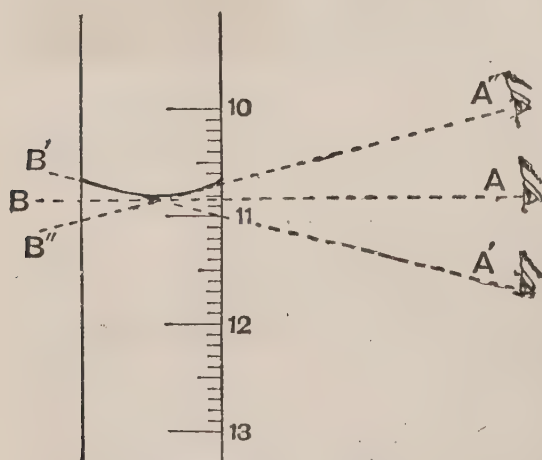


FIG. 12.

With a convex meniscus the top of the curve is taken, as is done when reading a barometer.

Exp. 5 will also have shown that the position of the eye makes a considerable difference in the reading. The true reading is only obtained by having the *line of sight perpendicular to the*

plane of the scale. as shown by *AB* in Fig. 12.

Any error caused by the wrong position of the eye is called the **error of parallax**, and is liable to be made in reading any scale.

Graduations on measuring vessels. The scale etched on measuring vessels is arranged to show either (a) the volume of the liquid the vessel *holds*, or (b) the volume it will *deliver* on pouring out the liquid into another vessel.

A measuring jar may be graduated in either way, or in both ways; for accurate work it is important to know which method has been used.

The graduation marks are liable to slight inaccuracy of position. For very exact work they have to be carefully tested beforehand, and a table of corrections made.

Exp. 6. To test the accuracy of a measuring jar.

Required:—200 c.c. jar, small flask, glass tube, balance.

DIRECTIONS. Weigh a small flask, using the rider. Carefully pour distilled water into the jar, adjusting the level with a glass tube, until the scale reads 20 c.c. from the bottom.

Transfer the water to the flask; wait a few seconds for the last drops to fall in, but do not shake out any which do not drop out naturally.

Weigh the flask again and ascertain the weight of the 20 c.c. of water. Calculate the true weight of 20 c.c. of water, being given that 1 c.c. weighs 0.999 g. when the temperature is between 10° C. and 18° C.

LABORATORY RECORD. Record of weighings.

- Questions:—*(i) Is the jar accurate for the first 20 c.c. or not? If not, is the 20 c.c. mark too high or too low?
- (ii) How would you test the rest of the scale on the jar?
- (iii) To what fraction of the scale unit can you safely estimate the volume that an accurate jar would deliver?
- (iv) If you wished to transfer very small volumes, say 3 or 4 c.c. correct to 0.1 c.c., what modification in the construction of the vessel is necessary?

Exp. 7. To use a burette.

Required:—Burette clamp and stand, grease, rubber band, small porcelain dish.

DIRECTIONS. *A.* Examine a burette, and **note**—

- (a) the unit of volume used as the basis for graduation,
- (b) from which end the graduations begin,
- (c) the volume between two successive scale *numbers*,
- (d) the volume between two consecutive scale *lines*,
- (e) the tap and nozzle.

N.B.—*A burette is graduated to deliver the volume indicated by the scale.*

B. Find whether the tap works smoothly—if not, grease it slightly, but prevent the grease from getting into the boring.

Fasten a rubber band on the tap handle, pass it under the nozzle and over the other end of the barrel of the tap. This prevents the tap from slipping horizontally.

Clamp the burette to a stand, with the scale to the front, and the tap on the right-hand side.

Adjust it to a vertical position by a plumb-line, i. e. a piece of thread fastened to a small piece of lead.

Place a small funnel at the top, and pour in water until the level is *above* the zero mark. Remove the funnel.

Run out a little water into a dish, so as to fill the tap-boring and nozzle.

Adjust the level to the 43 c.c. mark,* using a black paper card, and avoiding errors of parallax. *Submit it for inspection.*

C. Allow the water to run out, drop by drop, until 30 drops have escaped. Read the level again correct to 0.1 c.c., and estimate to 0.01 c.c. Find the volume of water thus run out.

* See note at bottom of page 21.

- Calculate (a) the volume of 1 drop in c.c. ;
(b) the number of drops in 1 c.c.

LABORATORY RECORD. Diagram of burette and tap showing the features noted in A.

Enlarged diagram of appearance of meniscus as it is seen with the card behind it.

Readings, &c.—

2nd reading, after escape of 30 drops =	c.c.
1st „ before „ „ „ =	c.c.
Vol. of 30 drops . . . =	c.c.
∴ vol. of one drop =	c.c.
No. of drops in 1 c.c. =	.

[In the Fair Notebook insert a *full* description of B and C.]

- Questions:—(i) Why is it necessary to run a little liquid out of the burette before noting the first reading?
(ii) Why is it necessary to have the burette vertical?
(iii) Will a slightly wrong position of the eye make as great an error in reading a burette as in reading a measuring jar? Give a reason.
(iv) Which of the two do you consider the more accurate—a burette or a measuring jar, and why?

Exp. 8. To test the accuracy of a burette.

Required:—Burette, small corked flask, balance.

DIRECTIONS. Use a small weighed flask provided with a cork as in Exp. 6.

Having filled the burette with distilled water and adjusted the level to the zero mark, run 5 c.c. into the flask, cork it and weigh, using the rider.

Record results and **note** the temperature of the water.

Run in 5 c.c. more water and reweigh.

Repeat this and find the weight of 15 c.c.

LABORATORY RECORD. Arrange results thus :—

Temperature of water	=	° C.
A. Weight of corked flask + 5 c.c. of water . =		
Weight of corked flask . . . =		
∴ weight of 1st 5 c.c. . . . =		
B. Weight of corked flask + 10 c.c. of water =		
" " " + 5 " " =		
∴ weight of 2nd 5 c.c. . . . =		
C. Weight of corked flask + 15 c.c. of water =		
" " " + 10 c.c. " " =		
∴ weight of 3rd 5 c.c. . . . =		

Calculate the *average* weight of 1 c.c. of water.

- Questions :—(i) Do you get the same weight for each lot of water ?
 (ii) Is the burette accurate ? (Refer to table below.)
 (iii) Is the burette consistent ?
 (iv) Why was a *corked* flask used ?

The following table gives the weight of 1 c.c. of pure water for temperatures between 11° C. and 20° C. correct to 0.1 mg.

gram.	gram.
11° C. 0.9996	16° C. 0.9990
12° C. 0.9995	17° C. 0.9988
13° C. 0.9994	18° C. 0.9986
14° C. 0.9993	19° C. 0.9985
15° C. 0.9992	20° C. 0.9983

Calibration of measuring vessels. For very accurate work the accuracy of each graduation mark is tested by methods similar to that used above and a table of corrections made and kept for future use. The process is called 'calibration'.

Exp. 9. To use a pipette and a standard flask.

Required:—A pipette, two small dishes, 100 c.c. standard flask.

DIRECTIONS. *A*. Examine a pipette, noting its shape, the scratch on the stem, and the capacity marked on the bulb.

N.B.—The volume indicated on the bulb is what the pipette will *deliver*.

B. Suck up water from a dish into the pipette until its level is *above* the scratch on the stem.

Press a finger quickly on the top without letting the water-level sink below the mark.

Hold the pipette over the dish with the scratch level with the eye. Relax the pressure of the finger until the lower edge of the meniscus is just level with the scratch. (Practise this until it can be done easily.)

Now hold the end of the pipette over a dry dish and allow the water to run out.

Hold the pipette over the dish for three or four seconds longer, and touch the surface of the water with the end of the pipette, thus causing a little more water to run out, but *do not blow out the residual water*.

The dish now contains 10 c.c. of water.

C. Examine and draw a diagram of a standard flask.

It is used to *hold* a known volume of liquid.

LABORATORY RECORD. Diagram of pipette showing meniscus. [For Fair Notes a *full description* of *B* in your own words is to be given.]

Questions:—(i) Why is the temperature often marked on pipettes, standard flasks, &c., as well as the volume?

(ii) Make a list of the vessels you have used which (a) *hold* a given volume, (b) *deliver* a given volume.

(iii) How would you test the accuracy of (a) a pipette, (b) standard flask?

QUESTIONS ON CHAPTER II.

N.B.—*Refer to note before the questions on page 10 before answering these questions.*

1. Draw a diagram of a balance from memory, naming the various parts.

2. Why is the beam of a balance taken off its bearings when not in use? How is it done?

3. Describe how you could find the *accurate* weight of an object on an imperfectly adjusted balance without readjusting it.

4. Explain the use of (*a*) the knob over the middle of the beam of a balance, (*b*) the rider.

5. Why is it necessary to avoid draughts when weighing, and why should the beam be swinging and not stationary when judging whether the weights balance the object?

6. Write down, from memory, the chief rules to be observed in weighing an object. Why should weights never be fingered, and why should objects to be weighed always be cold?

7. Describe *clearly and fully* a burette, and state how you would use it to deliver 10 c.c. of liquid into a flask. Give all necessary precautions to ensure accuracy.

8. What is the limit of accuracy of (*a*) the measuring jar, (*b*) the burette you have used? What means did you take to avoid mistakes in reading due to (*a*) the meniscus, (*b*) to parallax?

9. Describe *clearly and fully* a pipette and the method of using it.

10. What is meant by *calibration*? How would you calibrate a pipette?

CHAPTER III

SOME PROPERTIES OF LIQUIDS. SOLUTIONS

Preliminary Questions.* 1. What happens to a lump of sugar when put in a glass of water and allowed to stand for some time?

2. What difference would there be in the effect if the water were (a) stirred, (b) heated?

3. If the glass contained *very little* water, and several lumps of sugar, would the same effect be observed?

4. Why does sea water taste like salt?

5. Can salt be got from sea water? If so, how?

6. If you were given some muddy water, how would you separate the water from the mud? [When particles of mud or other solids are floating about in a liquid, they are said to be 'suspended' in the liquid.]

7. What do you understand by the words 'solution', 'solvent', and 'dissolve'?

8. Distinguish between 'melting' and 'dissolving'.

9. Do you know of any cases where two liquids after being shaken together and then allowed to stand (a) do, (b) do not, separate into two layers? If so, state how you would attempt to separate the two liquids in each case.

10. Can one liquid be said to dissolve in another?

Exp. I. To separate liquids from suspended solids.

Required:—Test-tubes, sand, sawdust, filter-paper, funnel.

DIRECTIONS. A. Take two test-tubes, put a little sand into one and a little sawdust into the other, fill each up

* Copy out and answer as many of the questions as possible in your Fair Notebook, from your general knowledge, and without any help.

with water and shake. Allow them to stand and **note** whether the suspended particles settle to the bottom of the tube or not. If they do so, all that is necessary is to pour off the water into another vessel, leaving the solid in the tube. This process is called **decantation**, and the liquid is said to have been decanted from the solid residue.

B. If the solid does not settle, the mixture must be filtered as follows:—Take a circular piece of filter-paper, bend it exactly in two, and then in two again. Open it out into a cone, and place it in a glass funnel, so that it fits well. Moisten the paper with a little water to make it keep its place, and put the stem of the funnel in the mouth of another test-tube. Shake the tube containing the mixture and pour its contents on to the filter-paper. This process is called **filtration**; the particles of water get through the spaces between the fibres of the paper, but the solid particles are too large to do so. Sometimes muslin, charcoal, a plug of wool, &c., are used instead of paper for filtering. Writing-paper will not do, because the spaces have been filled up with 'size'. The liquid which passes through a filter is called the **filtrate**.

LABORATORY RECORD. Diagrams to illustrate decantation and filtration.

Questions :—(i) What is the object of (a) decantation, (b) filtration?
(ii) Define the terms decantation and filtration.

Suspended and dissolved solids. When sand and sawdust are stirred with water, even for a long time, they remain in the solid state and are said to be *suspended* in the water. On the other hand, if salt or sugar be treated in the same way they disappear from view, lose their solid form, mix completely with the water, and are said to be *dissolved* in the water. If there is not enough water to dissolve all the solid, the excess remains suspended.

Exp. 2. To obtain a dissolved solid from its solution.

Required:—Brine, filter, small porcelain dish, sand-bath, lens.

DIRECTIONS. *A.* Filter some brine and **note** the taste of the filtrate.

B. Half fill a small porcelain basin with brine, place it on wire gauze over a tripod and heat it with a *small* flame until no more liquid remains.

Note what happens when most of the liquid has gone.

C. Repeat *B*, but use a sand-bath (i.e. an iron tray containing sand). When about five-sixths of the liquid has gone, turn out the lamp and leave the hot sand to finish the evaporation.

D. Repeat *B*, using a steam-bath (i.e. heat the dish by means of steam arising from boiling water) as in Fig. 13.

E. Repeat *C*, but only evaporate about three-quarters of the liquid. Remove the dish from the sand-bath and let it cool. (If no solid appears when cold, evaporate it a little more.)

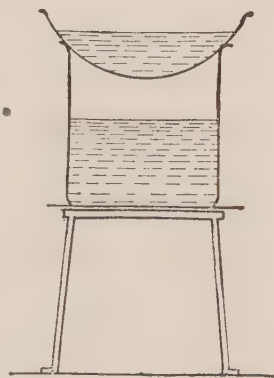


FIG. 13.

Note the appearance of the residue and compare it with that of the residue in *B*. (Use a lens.)

F. Find whether tap-water contains dissolved solids by evaporating a little on a sand-bath.

LABORATORY RECORD. Diagrams showing sand-bath, steam-bath, and notes on the results.

Questions:—(i) Does filtration remove a dissolved solid?

(ii) Which method of evaporation is (a) quickest, (b) slowest?

(iii) Which method would you use if you wanted to lose *none* of the solid?

(iv) In what way does the solid residue in *E* differ from that in *B*?

(v) How would you modify the process of evaporation so as to recover the solvent as well?

Evaporation is the process by which a liquid is converted into its vapour. If the liquid originally contained a dissolved solid, the solid remains in the vessel, but otherwise there is no residue.

Use of sand-baths and steam-baths. A sand-bath is used in preference to gauze whenever it is desired to finish the heating *gently*, and to prevent the dissolved solid from spirting much. Spirting may occur even with a sand-bath, so that in quantitative experiments (i.e. where the solid is to be weighed afterwards) it is essential to use a steam-bath, even though it takes much longer; sometimes the evaporation of a solution can be begun on a sand-bath and finished on a steam-bath without losing any solid.

Note on solutions of solids. Exp. 2, *A*, showed that the particles of salt were so small that they got through the pores of the filter-paper as easily as did those of the water. Hence dissolved salt is in the liquid state, but separates out as a solid when the liquid (i. e. the solvent) is evaporated.

The term **solution** is used in two senses, viz. :—

- (1) the process by which a body is liquefied, by contact with a liquid (the solvent) with or without external heat. [Compare this with melting or fusion, which is the process of liquefying a solid by the action of heat alone.]
- (2) the product of the foregoing process is also called a solution, e.g. the mixture of the solvent and the liquefied dissolved body.

For example, when a little salt is shaken up with water the solid disappears from view and is said to have undergone *solution*; the resulting mixture is called a *solution* of salt. The dissolved solid is called the *solute*.

Distillation. Tap-water usually contains dissolved solids which would interfere with many chemical experiments. They are removed by distillation, a process by which a liquid is evaporated in a closed vessel and its vapour condensed and collected in a separate vessel or receiver. Any dissolved solids are left behind in the boiling-vessel or boiler.

Exp. 3. To obtain pure water from tap-water or solutions.

Required:—As in Fig. 14; solution of blue vitriol.

DIRECTIONS. The apparatus required for distillation consists of a flask or boiler (*C*), a Liebig condenser (*A*, *B*), and a receiver (*D*). *E* is an adapter and is only required for very volatile liquids. A current of cold water enters the condenser at *B* and leaves at *A* (Fig. 14).

Distil some tap-water or blue vitriol solution. Violent boiling should be prevented by turning down the lamp or by putting a few bits of pipe-clay into the boiler. Reject the first fifth of the distillate, which may be considered to have cleansed the apparatus, and stop boiling when four-fifths of the original liquid has been evaporated.

Note the reading of the thermometer when the bulb is placed for about five minutes—

- (a) in the vapour above the liquid;
- (b) in the boiling liquid.

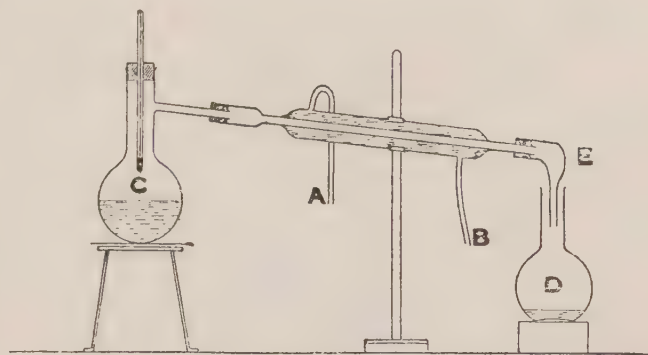


FIG. 14.

Also when the bulb is

- (c) drawn back above the liquid to first position;
- (d) wiped dry and replaced in the vapour.

Cork up the distillate in *D* and keep for the next experiment, which should be done on the same day. [If this is impossible the barometer should be read on both days, and the *same thermometer* used.]

LABORATORY RECORD. Diagram and observations *a*, *b*, *c*, and *d*.

Questions:—(i) Why does cold water enter at *B* and not at *A*?

(ii) How do you account for the differences in the temperatures recorded?

PROBLEM (III. 3). Investigate any large distilling apparatus in the laboratory. Draw a diagram, and write a full description of the process.

Exp. 4. To observe the boiling temperature of a pure liquid and of a mixture of liquids.

Required:—As in Fig. 15; absolute alcohol, clay pipe-stem.

DIRECTIONS. *A.* Arrange the apparatus as in Fig. 15, being careful not to clamp the tube too tightly. Place a small quantity (3 cm. deep) of the distilled water from Exp. 3 in the tube.

Use a *small* flame and heat to boiling, and allow to boil for a few minutes.

Note the temperature:—

(a) soon after vapour issues freely from the exit-tube;

(b) at intervals of a few minutes.

B. Repeat *A*, using a clean tube and absolute alcohol.

C. Add an equal volume of water to the alcohol left in the tube, put in two bits of clay pipe-stem, and repeat *A*.

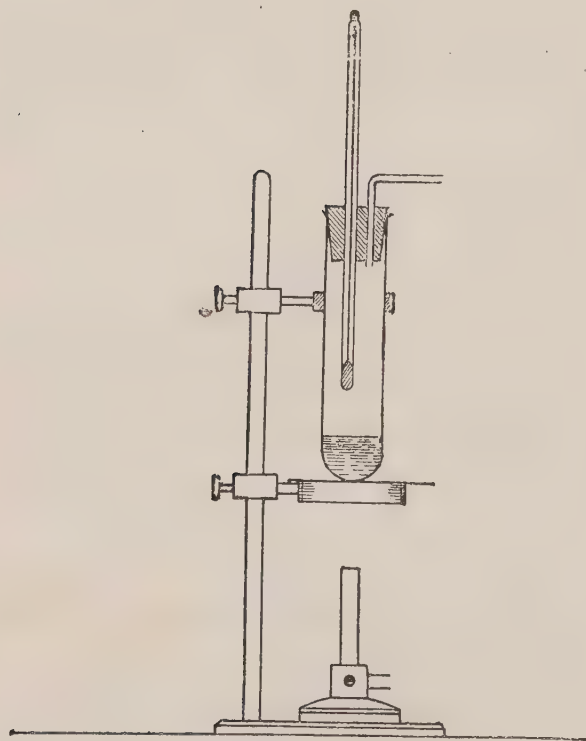


FIG. 15.

LABORATORY RECORD. Diagram of apparatus. Record of temperatures in *A*, *B*, and *C*.

Questions:—(i) Does the temperature alter during the boiling of (a) water, (b) alcohol, (c) the mixture of alcohol and water?
(ii) How can you tell whether a given liquid (a) is pure, (b) is a mixture of liquids, (c) contains dissolved solids?
(iii) How is the boiling temperature of (a) a solution, (b) a pure liquid found?

Boiling-points of solutions, mixed liquids, and pure liquids.

The details of the methods employed for the accurate determination of boiling-points (B.P.) of liquids are to be found in books on Heat. The following remarks require emphasis in connexion with their application in Chemistry. Exp. 4 will have shown that the temperature of the vapour from a solution is constant provided that none of the actual solution is in contact with the thermometer. This constant temperature is the B.P. of the solvent. The B.P. of the *solution* can only be found by immersing the bulb in the solution. If the bulb has once been wetted with the solution and then drawn up above the surface of the liquid, a temperature between that of the vapour and the solution is recorded, until all the solution has dropped back into the vessel.

The temperature of the vapour from a *pure boiling liquid* is constant, provided the atmospheric pressure is constant. If the latter increases the B.P. is higher and vice versa. The temperature of a pure boiling liquid at its surface will not differ much from that of the vapour unless some of the substance of the vessel has been dissolved. But if the bulb is placed deep in the liquid the B.P. rises, because the pressure is greater below the surface. Hence the usual custom in taking the B.P. of a pure liquid (or in testing whether a liquid is a mixture or not) is to *keep the thermometer bulb well above the surface*.

In a mixture of liquids boiling usually begins near the B.P. of the most volatile liquid, and the temperature goes on rising to about the B.P. of the least volatile. Hence if the temperature of the vapour from a boiling liquid is not constant, the liquid is a mixture. The converse is, however, not always true. There are certain mixtures which cannot be separated by distillation.

Exp. 5. To separate the soluble from the insoluble portion of a mixture of solids, and to find the percentage weight of each present.

Required:—Mixture of potassium chromate and calcium carbonate (pptd.) in known proportions, beaker, weighed dish, gauze, funnel, tripod, balance.

DIRECTIONS. Weigh a small beaker, using the rider. Add about 2 g. of the given mixture and then weigh exactly. Half fill the beaker with distilled water, stir and warm to dissolve the yellow chromate.

Weigh a small porcelain dish and then weigh a filter-paper. Fix a filter over the dish, moistening the paper with water. Allow the solid in the beaker to settle and pour the yellow liquid down a glass rod on to the filter. Add more water to the beaker, stir, allow to settle, and decant off the liquid on to the filter. [This is called **washing by decantation**: the insoluble white solid is gradually being washed free from the yellow liquid. This is quicker than **washing by filtration**, i. e. pouring both liquid and solid on to the filter at first, for the solid prevents the liquid running through quickly.] Wash once more by decantation, replacing the basin by another if full. Put the first basin on a steam-bath to evaporate. Add more water to the beaker, stir, and pour out both solid and liquid on to the filter. Wash the last traces of solid out of the beaker by means of a wash-bottle, the beaker being half inverted over the filter. [N.B.—None of the white solid nor of the yellow liquid is to be lost—if this occurs begin again.] Wash the solid on the filter till no trace of yellow remains.

Evaporate the rest of the filtrate on a sand-bath to about a quarter of its bulk, then pour the liquid into the first basin on the steam-bath, rinsing it out with a little fresh water. All the yellow solution must be put in the first basin, and the evaporation finished on a steam-bath. Meanwhile put the funnel and filter-paper to dry in an air oven. When *apparently dry*,

weigh (use rider) the paper with the white solid, being careful not to spill any. Put it back to dry for 10 min. more and reweigh. Repeat this until two consecutive weighings agree, for this is the only means by which you can tell that the solid is really dry.

When the yellow solid *seems* dry, wipe the basin underneath and weigh it (use rider). Place in an air-oven at 110°C for 10 min. and reweigh. Continue until two consecutive weighings agree.

LABORATORY RECORD. Enter the weighings in a well-arranged schedule, previously made. Find the weights of the soluble and insoluble solids and add them together. Find whether the total is equal to the weight of mixture taken or not. Calculate the percentage weight of each, i.e. suppose you started with 100 g. of the mixture.

Questions:—(i) Is it necessary to weigh both solids in order to find the percentage of both in the mixture?

(ii) Which of the two solids could be separated and weighed quickest?

(iii) Mention the chief difficulties you found in performing the experiment.

(iv) What percentage of the weight of the mixture did you lose (if any)?

PROBLEMS (III. 5). Find the percentage of insoluble matter in the given mixtures of—(1) finely powdered *shellac* and *silica*; (2) *sand* and *sugar*.

Fractional Distillation. To separate the components of a mixture of liquids the mixture is distilled and the receiver is changed after every rise of 5 or 10 degrees. On submitting the first and last of these fractions of the distillate, separately, to further distillations and collecting again in fractions, a pure specimen of each can often be obtained.

Exp. 6. To test the solubility of various solids in cold and hot water.

Required:—7 test-tubes, 3 basins or watch-glasses, (a) nitre, (b) borax, (c) plaster of Paris, (d) lime, (e) chalk, (f) white sand, (g) blue vitriol, (h) Epsom salt, (i) sulphur, (j) iodine, (k) paraffin wax, (l) camphor, (m) powdered charcoal, (n) powdered glass.

DIRECTIONS. [Each member of the class should try at least seven of these solids, starting with (a) or (b), and then take the *alternate* ones.]

A. Use a test-tube half full of distilled water, add an *extremely small** quantity of the solid, and shake.

Note whether it dissolves or not. If it does, add a little more and shake again until the last portion remains in the solid state.

Note roughly how much dissolves, so as to compare the solubility of the different substances you use.

B. Warm the tube. **Note** whether the solubility increases or not.

If any substance seems insoluble, even after heating, filter it, and rapidly evaporate some of the filtrate in a small basin or watch-glass over a sand-bath to find whether it is really *quite insoluble* or only *very sparingly soluble*.

LABORATORY RECORD. Enter observations thus:—

Name of substance.	Cold water.	Hot water.	Other observations.
	(State whether it seems very soluble, fairly soluble, or insoluble.)	(Enter as under cold water, and also state whether the solubility seems to increase or not.)	(Colour of solution and any peculiarities noticed.)

* As much as will cover the letter O. If more is taken at first, much time will be wasted.

Exp. 7. To ascertain the solvent power of other liquids.

Required:—Clean sand, sulphur, paraffin wax, iodine, powdered charcoal, chalk, methylated spirit, petrol, benzene, 6 test-tubes, steam-bath.

DIRECTIONS. Repeat Exp. 6, using four of the above solids with each of the liquids mentioned.

First try with the liquid at the air temperature, and afterwards warm it by putting the tube in a bath of hot water.

Precaution:—*None of these liquids must be heated by a flame; all lamps must be turned out.*

LABORATORY NOTES. Scheme for observations, as in Exp. 6.

Questions:—(i) What substances appear insoluble in all the liquids you tried?

(ii) Name those insoluble in water but soluble in some other liquid. Give names of liquids.

(iii) Give reasons for the precaution.

PROBLEM (III. 7). Test the solubility of sulphur in *cold* carbon bisulphide.

Filter and allow to evaporate in a draught cupboard at the air temperature.

Saturated Solutions. The previous experiments will have shown (*a*) that solids differ very much in the extent to which they will dissolve in a given quantity of the same liquid, and that some are insoluble; (*b*) that a solid may be soluble in one liquid but insoluble in another; (*c*) that increase of temperature usually increases the degree of solubility of the solid. The latter statement is true of very many solids, but some (e.g. common salt) do not become appreciably more soluble when the solvent is hot, and a few become less soluble.

When a given quantity of solvent has dissolved as much of a substance as it can at a given temperature, the solution is said to be **saturated** for that temperature, or, in other words, *a saturated solution is one which is incapable of dissolving any more of the substance without alteration of the temperature.*

A solid dissolves much more quickly if powdered than if in lumps, as a larger surface is exposed to the liquid. Similarly the speed of solution is increased by stirring or shaking, since fresh portions of the unsaturated solvent are brought into contact with the solid.

Exp. 8. To make a saturated solution of alum and to observe the effects of heating and cooling it.

Required:—Alum, test-tubes, thermometer, filter.

DIRECTIONS. *A.* Take half a test-tubeful of water, add some alum, and shake well. If it all dissolves add more. Take the temperature of the solution and notice whether it is the same as that of the air or not. [Usually there is a fall of temperature when a solid dissolves.] If not, warm it until it is, adding more solid if none is visible in the tube.

When the temperature is right and there is a fair amount of visible solid after the mixture has been shaken for some time, decant or filter so as to get the *clear* solution in another tube without visible solid. This is a saturated solution of alum at the air temperature.

B. Heat the solution in a small flame and **note** whether it is still saturated or not, by adding more alum and observing if it dissolves. Aim at getting it saturated at some definite temperature, say 40°C . Cool the solution by placing the tube in cold water. **Note** what happens.

LABORATORY RECORD. Observations. For Fair Notes a *careful* description of *A*.

Questions:—(i) Is a cold saturated solution of alum in water still saturated when warmed?

(ii) *Explain* the effect of cooling the hot saturated solution.

(iii) Do you think the same effect would be noticed if the cold saturated solution had been heated without further addition of alum, and then cooled?

Definition of Solubility. Exps. 6 and 7 only gave a *rough* idea of the degree of solubility of the solids in the liquids employed. In order to obtain an *exact* idea of the extent of the solubility of solids, some definite mode of comparison must be decided upon, and a definite meaning given to the word 'solubility'. This has been done as follows:—The **solubility of a solid in a liquid** at a given temperature is the number of grams of solid which dissolve in 100 g. of the liquid to form a saturated solution at that temperature.

It is useful to remember that solutions in water are often called *aqueous solutions*, and those in alcohol 'alcoholic solutions' or *tinctures*, e. g. tincture of iodine.

Exp. 9. To determine the solubility of a solid in water at different temperatures.

Required:—2 flasks of 50 c. c. capacity, weighed dish, water-bath, potassium chlorate, tile, thermometer.

DIRECTIONS. *A. At the temperature of the laboratory.* Take about 30 c.c. of distilled water in a flask and make a saturated solution of the powdered solid, as in Exp. 8 *A*.

Filter (or decant) the clear solution into another flask and **note** its temperature.

Pour a small quantity into a clean weighed dish.

Weigh again. Evaporate to dryness on a steam-bath.

When apparently dry, wipe the outside of the dish, allow it to cool on a tile, and weigh again when quite cold. Replace in an air-bath at 110°C . for 10 min. and weigh again until two consecutive weighings agree.

*B. At some other temperature.** Take a water-bath, large enough to hold the flask; and heat the bath a little above the given temperature.

Turn the flame low to keep the temperature constant.

Now make a saturated solution of the solid at this tem-

* In this experiment it is advisable for pupils to work in pairs, each pair taking a different temperature at intervals of 5 or 10 degrees between 15°C . and 65°C . The general results can be plotted on squared paper.

perature. Proceed as in *A*, but keep the flask in the bath, add solid gradually, and shake till no more dissolves.

Precaution :—*Be quite sure that the liquid is saturated.*

Weigh a small corked flask.

Let the excess of solid settle, **note** the exact temperature of the solution, and quickly transfer some of the *clear* solution (about 10 c.c.) into the weighed flask.

Cork it, cool, and then weigh.

Pour the contents of the flask into the weighed porcelain basin, and rinse out the flask with a little distilled water until all the solid has been transferred to the basin.

Evaporate to dryness and weigh as in *A*.

LABORATORY RECORD. Enter results in each case as follows :—

Temperature of solution	=	° C.
Weight of dish * + solution	=	g.
Weight of dish *	=	
<i>Solution weighs</i>		g. (<i>X</i>)
Weight of dish + dry solid	=	g.
Weight of dish	=	g.
<i>Solid left weighs</i>		g. (<i>Y</i>)
<i>Weight of water</i> = <i>X</i> - <i>Y</i>	=	g. (<i>Z</i>)

Calculate the weight of solid dissolved by 100 g. of water.

Ask what the correct results are, and record your error (if any).

Record any difficulties.

Plot the general results of the class on squared paper, marking the temperatures horizontally and the solubilities vertically. Choose units so as to make the curve joining the points cover the whole of the paper.

PROBLEMS (III. 9). 1. Determine the solubility of *common salt* or *Epsom salt* at 20° C., 40° C., and 60° C.

2. Find the solubility of *paraffin wax* in *petrol* at the temperature of the laboratory, remembering that the wax melts below 100° C., and petrol boils at about 45° C.

* In *B*, corked flask.

QUESTIONS ON CHAPTER III.

1. Answer any of the *preliminary questions* (p. 29) which you were unable to answer or answered incorrectly before. [These should be written in your Fair Notebook after Exp. 9.]

2. By what methods may (a) suspended solids, (b) dissolved solids, be obtained free from the liquid containing them? Compare the advantages of the methods both for (a) and (b).

3. Describe and explain the use of (a) a sand-bath, (b) a steam-bath, (c) an air-oven.

4. Explain clearly and concisely what is meant by (a) Decantation, (b) Evaporation, (c) Filtration, (d) Distillation.

5. Give an account of the process and objects of distillation.

6. How can the percentage proportions of a soluble and insoluble solid in a mixture be determined accurately?

7. Explain fully what is meant by the term *saturated solution*, and define the term *solubility of a solid*.

8. Explain in detail how you would ascertain the solubility of a solid in water at 50°C .

9. 10 c.c. of a solution of salt in water (at the air temperature) weighed 11.8 g. After evaporation 3.04 g. of salt remained. Calculate the solubility of salt at this temperature.

10. Draw a solubility curve for nitre from the following data, marking the temperatures horizontally:—

Temperature	0°	10°	20°	30°	40°	50°	55°
Solubility .	13	21	31	45	64	86	100

11. From the curve drawn in the last question find—

(a) the solubility of nitre at 45° ; (b) the temperature at which 100 g. of water are saturated by 25 g. of nitre.

12. Draw a curve for Epsom salt from the following data:—

Temperature	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Solubility .	26.9	31.5	36.2	40.9	45.6	50.3	55	59.6	64.2	68.9	73.8

13. If 173.8 g. of the solution saturated at 100°C . are cooled to 15°C ., what weight of Epsom salt would separate out?

14. The following data give the solubility of lead chloride at various temperatures :—

Temperature	0°	10°	20°	40°	55°	80°
Solubility .	.8	.946	1.18	1.7	2.1	3.1

Draw a curve and estimate the solubility at 19° C. and at 30° C.

15. 100 g. of water are shaken at 40° C. for 15 minutes with 40 g. of a mixture of salt and lead chloride. The whole of the lead chloride is dissolved and 2 g. of salt are left undissolved. What was the composition of the mixture used? Solubility data for common salt :—

Temperature	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Solubility .	35.7	35.8	36	36.3	36.6	37	37.3	37.9	38.4	39.1	39.8

CHAPTER IV

SOME PROPERTIES OF SOLIDS CRYSTALLIZATION

Distinction between solids and liquids. Solids differ from liquids in possessing a definite shape, while liquids take up the shape of the containing vessel, except at the free surface, which is level when not quite close to the vessel. The particles of a solid cohere and preserve its shape, but the force of cohesion between the particles of a liquid is very slight, so that a liquid has the power of 'flowing', which a single piece of solid has not. Solids can usually be converted to liquids by the action of heat, and conversely, when a liquid is sufficiently cooled it solidifies.

The shape of a solid produced by cooling a liquid, e.g. the freezing of a film of water on a window, is often of a definite kind and peculiar to that solid. Any solids which are capable of forming into these definite geometrical shapes or crystals are called *crystalloids*, but there are some, such as resin and gum, which never crystallize however favourable the conditions may be; these are called *colloids* (Latin *colla*, gum), and are said to be *amorphous*, which means 'without definite shape'.

Exp. I. Examination of common crystals.

Required:—Crystals of calcite, quartz, iron pyrites, selenite, pestle and mortar, protractor and ruler, angle measurer (see Fig. 16).

DIRECTIONS. *A.* Examine the crystals and **record** results thus:—

Name of crystal.	Locality.	Name and sketch of shape.	Colour.	Transparency.	Hardness.	Other observations.
	Say where you have previously seen a specimen.	Cube, rhomb, or prism, &c.		Say whether transparent or opaque.	Say whether it is scratched by steel or not.	

B. Take a crystal of calcite and break it as gently as possible with a pestle in a mortar. **Note** whether it breaks into smaller crystals of the same shape or not.

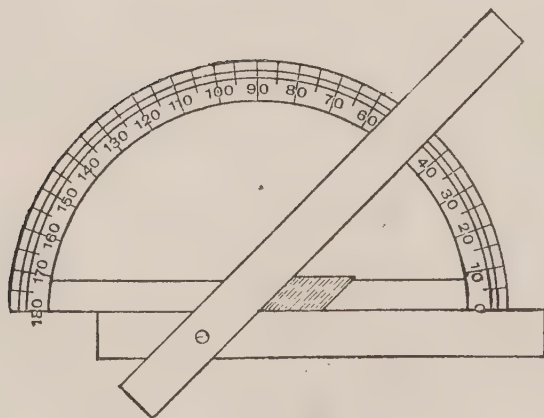


FIG. 16.

Try to cut one bit with a knife in different directions. **Note** in which directions it *cleaves* easily.

C. Pick out two perfect crystals of calcite, one large and the other small. Measure the angles of

each in degrees, by means of a protractor and angle measurer, as shown in Fig. 16. **Record** as below:—

Calcite.	Large crystal.	Small crystal.
1st acute angle =		
2nd „ „ =		
1st obtuse „ =		
2nd „ „ =		

LABORATORY RECORD. Enter observations as shown above.

Questions: – (i) Are all crystals transparent? Give examples.

(ii) Are all crystals colourless?

(iii) If a large crystal of calcite had been cut into a sphere would you say (a) that it was still a definite crystal, or (b) that it had a crystalline structure? Give reasons.

(iv) How would you try to find out whether a rough lump of a substance was crystalline or not?

(v) How would you test a small chip of crystal to find whether it was quartz or a bit of transparent calcite?

Notes on the crystals examined. *Calcite* is very common in limestone districts, and is often called ‘spar’. *Quartz* or *rock crystal* occurs in granite and in the veins of other rocks. *Iron pyrites* is found crystallized on a large number of rocks. It occurs as a yellow film in coal. *Selenite* occurs in beds of clay, e.g. in Oxford clay.

You should examine other crystals in a museum.

Exp. 2. To study the conditions of crystal formation.

Required:—Small flask, test-tube, basin, blue vitriol, porous plate.

DIRECTIONS. *A.* Make a saturated solution of blue vitriol at about 40° C. (See Exp. 8, p. 40.) Decant half of the clear liquid into an evaporating basin, and let it stand on the bench until it is quite cold. Whilst it is cooling proceed with *B.*

B. Cool the remainder of the warm solution by floating the basin in a vessel of water, stirring vigorously with a glass rod all the time.

C. Decant the clear cold liquid from *A* into another basin, cover the basin with a filter-paper, and set it aside to evaporate slowly till the next lesson. Transfer the solid to a porous plate by means of a glass rod.

LABORATORY RECORD. Notes of results; sketch of a single crystal.

Questions:—(i) Do the largest crystals form when (*a*) the solution is cooled slowly or quickly, (*b*) the solution is agitated or still?

(ii) Why are no crystals formed from a cold unsaturated solution which is kept corked up?

(iii) Would crystals form from a cold saturated solution which is kept corked up? Give a reason.

(iv) What would be the best way to grow a large crystal?

At the following lesson the solution set aside must be examined, and notes as to the size and a sketch of the shape of any crystals which have formed should be made.

PROBLEMS (IV. 2). 1. Obtain and make a drawing of good crystals of any of the following substances:—alum, chrome alum, nitre, Glauber's salt, lead nitrate.

When crystals have formed in the saturated solution, select a single well-formed one, place it in a clean vessel, and pour upon it the clear cold saturated solution. Cover with paper, and leave the solution to evaporate slowly, examining and turning the crystal over from time to time, removing others which form.

If more of the saturated solution is added from time to time a large crystal may be grown.

2. Grow a large crystal as in Problem 1, but suspend a small piece of glass rod by a thread in the clear warm solution. Leave a good crystal on this for the second beaker and grow the large one round it. Use *bichromate of potassium*.

Best conditions for crystallization. Exp. 2 will have shown that the best crystals form when a saturated solution is allowed to cool and evaporate very slowly without shaking. This is because the solid which gradually comes out of solution as evaporation proceeds, will develop itself on a crystal already formed and so increase its size, rather than form an independent crystal. Shaking and rapid evaporation or sudden cooling prevent this.

It is also necessary that the crystal shall have an equal chance of growing on all sides.

In Nature these conditions are not often satisfied, so we find minerals in crystalline masses but with few perfect crystals.

Supersaturation. If a hot saturated solution is kept quite still and cooled very slowly, it sometimes does not crystallize until it is shaken or a small crystal of the solid dropped in. Such a solution is said to be *super-saturated*.

Exp. 3. The effect of heat on blue vitriol crystals.

Required:—Hard-glass tube, &c., as in Fig. 17. gauze, watch-glass, thermometer, balance, 6 test-tubes, absolute alcohol, turpentine.

DIRECTIONS. *A.* Put about 25 g. of *small dry* crystals of blue vitriol into a dry tube, and arrange as in Fig. 17.

[If the tube is of thick glass, wrap it with one layer of wire gauze.]

Heat the blue solid with a *small* flame, carefully moving it to and fro along the tube, but *avoid* burning the cork.

Note all that happens.

Keep the whole tube warm till the blue colour has just gone.

Lift the exit-tube out of the receiver *before* taking away the flame. Examine the solid to see whether it is still crystalline, then cork it up in a small tube, label, and keep it for *C*.

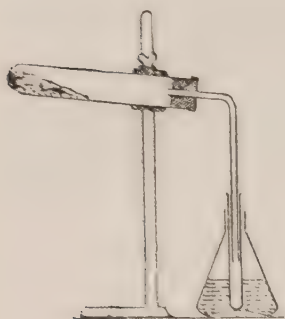


FIG. 17.

B. Try to identify the liquid.

Note its colour and smell (if any); see whether it flows about readily (i.e. whether it is *mobile* like water or alcohol) or whether it is *viscous* (like olive oil or treacle).

Find its density* by weighing 5 c.c. in a corked flask.

Note whether a residue is left on evaporation.

Note whether it boils at a constant temperature or not.

C. Place a little of the solid residue from *A* in each of five *dry* test-tubes, and in a watch-glass.

Add a few drops of water to No. 1; *pure* alcohol to No. 2; alcohol mixed with water to No. 3; turpentine to No. 4; some of the liquid used in *B* to No. 5.

* In case the quantity of liquid is very small, two or three pupils should combine for this and the following tests.

Note the effect in each case.

Leave the watch-glass with the powder in your cupboard till next lesson, and then **note** the result.

LABORATORY RECORD. Diagram ; full observations in *A*, *B*, and *C*.

Questions :—(i) What do you think the liquid is? Give reasons.

(ii) Is it a pure liquid or a mixture?

(iii) If you dissolved the solid residue from *A* in water and evaporated slowly, would you get blue crystals again? If so, do you expect them to be the same as those you started with, or different? [If in doubt, try it.]

(iv) For the detection of what liquid can the white residue (called white or anhydrous copper sulphate) be used?

PROBLEM (IV. 3). Investigate the products formed by *gently* heating either *washing soda*, *white vitriol*, *alum*, or *Glauber's salt*. Identify the liquid in each case.

Exp. 4. Some other effects of heat on solids.

Required:—Small ignition tubes, crystals of common salt, nitre, iodine, sal-ammoniac, lens.

DIRECTIONS. *A.* Use a few dry crystals of common salt or of nitre.

Heat in a dry tube (holding it in a sloping direction) in a small Bunsen flame.

Note (*a*) whether the solid *decrepitates* (i.e. breaks up violently, causing particles to fly off);

(*b*) whether the solid melts, and if so, what happens to the liquid;

(*c*) whether any liquid is deposited.

B. Use crystals of iodine or sal-ammoniac.

Note whether it melts, gives off a liquid or vapour.

Examine the deposit with a lens—breaking the tube if necessary.

LABORATORY RECORD. Observations *A* and *B*.

Questions:—(i) Do all crystals give up water on heating?

(ii) Arrange the crystals heated in Exps. 3 and 4 in three classes according to the effect of heat upon them.

PROBLEM (IV. 4). Devise a means for separating a mixture of salt and sal-ammoniac without using a liquid. Submit it for approval before trying it.

Water of crystallization. From Exps. 3 and 4 you will have seen that some crystals yield water on heating, while others do not. This water is called 'water of crystallization'; many solids will not crystallize unless water is present, and if they do, the crystals are of a different shape. Some solids form crystals of more than one shape, depending on the amount of water of crystallization.

Substances like common salt, nitre, and iodine, which contain no water of crystallization, are said to be *anhydrous*—a word derived from Greek, meaning 'without water'.

Volatility. On heating iodine or sal-ammoniac you will have observed that they do not melt (or melt only partially), but are turned almost at once into vapour, which condenses again in crystals on the cool part of the tube. The conversion of a solid into a vapour directly by heat, with subsequent collection of the re-formed solid, is called *sublimation*. The condensed vapour is called a *sublimate*, and a solid capable of undergoing sublimation is said to be *volatile*—a term also applicable to liquids of low boiling-points. Ordinary ‘smelling salts’ is an example of a volatile solid, and is called *sal-volatile*; camphor also vaporizes without previous melting.

Decomposition by heat. When blue vitriol is gently heated, water is given off and a white solid remains. If the water be mixed with the solid the colour returns and crystals can be re-formed. Thus heat decomposes the coloured solid into a white solid and water.

On heating the white solid further it suffers further decomposition, giving off a heavy vapour and leaving a black solid. Some substances like salt, sand, iodine, are not decomposed by heat.

Summary of the effect of heat on solids. The experiments show that on heating solids—

- (a) some are apparently *unaltered*, e.g. sand, porcelain;
- (b) some *melt* but re-form the same solid on cooling, e.g. salt;
- (c) some volatilize without melting and form sublimates, e.g. sal-ammoniac;
- (d) some give off water of crystallization without melting, e.g. blue vitriol;
- (e) some decompose further on intense heating, e.g. blue vitriol.

Exp. 5. To find the percentage loss of weight on heating solids.

Required:—Pestle and mortar, crucible (size 00), pipe-clay triangle, retort-stand, balance, blue vitriol or Epsom salt.

DIRECTIONS. *A.* Weigh a crucible and lid. *Half* fill it with the *powdered* solid, and reweigh. Place it on a pipe-clay triangle resting on the ring of a retort-stand, so as to be two inches above the top of the flame.

Heat with a small flame at first, and then with a larger one, but do not let the crucible get red-hot. Hold the lid with tongs just over the crucible, and watch what happens. Continue heating for about 15 min. (The lid may be replaced so as not to cover the crucible entirely.) Allow it to cool (with the lid on) and weigh when quite cold.

B. Heat again for 5 min. as before, cool, and weigh again.

Note whether there is any further loss in weight. (If so, continue till two consecutive weighings agree.)

LABORATORY RECORD. Diagram, observations, weighings in *A* and *B*.

Calculate what weight 100 g. of the solid loses on heating.

Questions:—(i) Why were the crystals first broken up in a mortar?

(ii) In *B* why had you to re-heat until two consecutive weighings were the same?

(iii) Are the contents of the crucible liable to increase in weight while cooling?

PROBLEMS (IV. 5). 1. Find the percentage weight of water of crystallization in (a) *soda crystals*, (b) *gypsum*, or (c) *white vitriol*.

2. Find the percentage weight of salt in a *mixture of salt and sal-ammoniac*.

Exp. 6. The effect of exposing certain solids to air.

Required:—3 watch-glasses, washing soda, blue vitriol, calcium chloride, balance.

DIRECTIONS. *A.* Select a few good dry crystals of (*a*) washing soda, (*b*) blue vitriol, and (*c*) lumps of calcium chloride. Label three watch-glasses, and place one kind of solid on each.

Weigh each with its crystal, and write the weight on the label. Put them aside till the next lesson, screening them from dust.

B. **Note** any change in appearance. Reweigh each and **note** any change in weight.

LABORATORY RECORD. Weighings in *A.* Observations and weighings in *B.*

Questions:—(i) Knowing that washing soda gives up water on heating, what do you think happened on leaving it in air?

(ii) What has happened to the calcium chloride?

(iii) How could you test the truth of your answer to (ii)? Try it, if approved.

PROBLEM (IV. 6). Find the effect of exposing lumps of *magnesium chloride*, *caustic soda*, *sodium sulphate*, and *alum* to the air for three or four days.

Efflorescence and deliquescence. When a solid gives off its water of crystallization on exposure to the air at the ordinary temperature, it is said to '*effloresce*'. Exp. 6 will have shown that washing soda crystals are efflorescent.

On the other hand, some solids (whether crystalline or not) absorb moisture from the air, and then dissolve in the water they have attracted. These are said to '*deliquesce*' in air or to be deliquescent solids. Both classes of substances should always be kept in closely stoppered bottles.

Advantage is taken of the action of deliquescent bodies

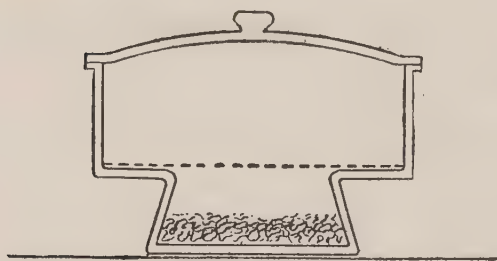


FIG. 18.

in order to provide a dry atmosphere in which a body liable to absorb moisture can be kept dry. An arrangement of this kind, shown in Fig. 18, is called a **desiccator** (to '*desiccate*' means to '*dry*').

A layer of some very deliquescent substance, such as calcium chloride (called a desiccating agent), is placed in the bottom of the circular glass vessel. Above this is a perforated zinc shelf on which the object to be kept dry is placed. The whole is closed with a glass lid with a ground rim, which is greased so as to be air-tight. The moisture in the air inside the vessel is absorbed by the desiccating agent, so that a deliquescent substance can be kept or cooled in the desiccator without any risk of its absorbing water vapour. Concentrated sulphuric acid is often used as a desiccating agent.

Exp. 7. To find the melting-point of a solid.

Required:—Melting-point tubes, rubber bands, palmitic acid, spermaceti, &c., as in Figs. 19 and 20.

DIRECTIONS. *A.* Use spermaceti; then palmitic acid.

Powder the solid, and introduce a small quantity into the melting-point tube* by pressing the open end of the tube into the powder and tapping the closed end on the bench.

Fasten the tube to the thermometer by a rubber band, so that the solid is opposite the bulb (Fig. 19). Clamp the thermometer with the bulb dipping into water (Fig. 20).

Place a small flame under the beaker, stir constantly, and watch for the first signs of melting. Then remove the flame from beneath the beaker, and stir vigorously; **note** the tem-



FIG. 19.

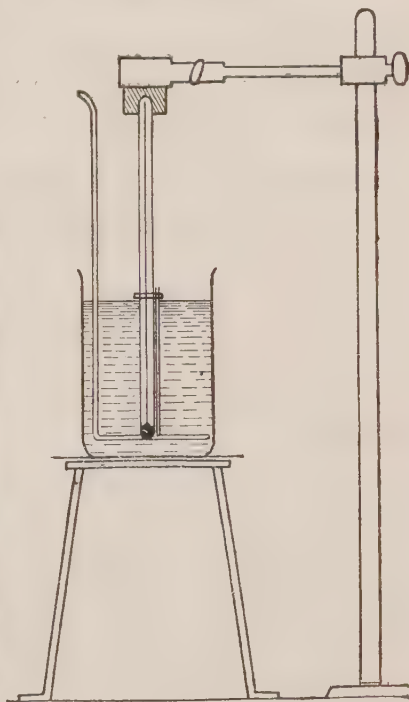


FIG. 20.

perature at which the solid shows the first signs of melting, and observe whether complete melting takes place at this temperature.

Do *three* experiments with each solid, and take the mean of the three results.

B. Mix a little spermaceti with about ten times as much palmitic acid, rub them together in a mortar, and repeat *A*.

[Over.]

* See p. 4.

LABORATORY RECORD. Diagram, short description of method, record of the three results obtained for each substance.

A comparison of the melting-points of pure palmitic acid and spermaceti with that of the mixture.

Questions :—(i) What conclusion would you draw as to the purity of a substance whose melting-point is not sharp?

(ii) What are the advantages of using a small quantity of the solid in a thin-walled narrow tube, and of having the solid close to the bulb of the thermometer?

If a substance melts at a temperature above 100°C. , some liquid other than water must be used to heat it. For this purpose olive oil may be used.

PROBLEM (IV. 7). Find the melting-point of *sulphur*, using a bath of *olive oil*. Submit your apparatus for approval before proceeding.

QUESTIONS ON CHAPTER IV.

1. State as many distinctions as you can between solids and liquids.

2. Explain and give examples of—(a) crystalloid, (b) colloid, (c) amorphous substances.

3. Explain as clearly as possible what you understand by the term '*crystal*'. Mention three crystalline substances, and give a sketch of the shape of the crystals.

4. Give an account of the best conditions for crystallizing a solid from its solution so as to obtain a well-formed crystal.

5. Well-formed natural crystals are generally found in the cavities of rocks, not in the solid mass. Account for this.

6. By what means would you ascertain whether a given liquid (a) contains water, (b) is pure water.

7. What is the meaning of the terms :—water of crystallization, decrepitation, sublimation, volatility?

8. Describe a method of determining the percentage of water of crystallization in a solid, mentioning all the precautions necessary to ensure an accurate result.

9. 1.68 g. of a crystalline solid weighed 1.07 g. after heating. Calculate the percentage weight of water of crystallization.

10. How can you find the proportions by weight in which a volatile and a non-volatile solid have been mixed? Give details.

11. Define the terms 'deliquescence' and 'efflorescence', and give examples of deliquescent and efflorescent bodies.
12. Explain the construction and use of a desiccator.
13. Describe a method for determining the temperature at which (a) a solid melts, (b) a liquid boils.
14. Explain a method of testing whether (a) a given liquid, (b) a given solid, is a single substance or a mixture.

CHAPTER V

SOME PROPERTIES OF GASES

Solids, liquids, and gases. Solids have a definite shape and a definite volume; liquids have a definite volume, but not a definite shape; gases have neither a definite shape nor a definite volume; they take the shape and volume of the containing vessel.

Gases and vapours differ in a very striking manner from both solids and liquids in their density, compressibility, and expansibility.

If the density of water be taken as unity, that of ice is 0.9 but that of steam at 100° is 0.0005. Water and ice are almost incompressible, but gases such as air and steam contract greatly when pressure is applied. Similarly, the expansion in volume which occurs when air, steam, and other gases are heated is enormous in comparison with the expansion of water and other liquids and solids.

Hence in measuring the volume of a solid or liquid no account is taken of the pressure upon them, and a difference of a few degrees in temperature makes only a very slight difference in their volume. On the other hand, in comparing the volumes of two gases or vapours it is necessary that they should be at the same temperature and pressure, or we must be able to calculate what volume they would occupy at the same temperature and pressure.

Exp. 1. To measure the expansion of air between 0°C. and 100°C.

Required:—Narrow tube attached to scale and containing a pellet of mercury as in Fig. 21, thermometer, ice, beaker on stand.

DIRECTIONS. Place the tube with its scale in a deep beaker of water, and add lumps of ice.

Stir with a thermometer until the temperature is reduced to 0°C. **Note** the volume* of the air and the temperature.

Heat the water to boiling, keeping all the tube below the mercury pellet in the boiling water.

Note the highest point to which the mercury rises and the B.P. of the water.

LABORATORY RECORD. Note the volumes and temperatures.

Expansion is measured by the increase in volume gained by unit volume at 0°C. when heated through 1°C.

Calculate as follows:—

$$\begin{aligned} \text{Volume at } 0^{\circ}\text{C.} & \quad = a \times k \text{ (where } k \text{ is area of} \\ \text{,, ,, } 100^{\circ}\text{C.} & \quad = b \times k \text{ cross-section)} \end{aligned}$$

$$\therefore \text{increase in vol. between } 0^{\circ} \text{ and } 100^{\circ} = (b - a) k.$$

$$\therefore \text{increase in volume (for } a k \text{ units of vol. at } 0^{\circ}\text{C.) for } 1^{\circ}\text{C.}$$

$$= \frac{(b - a) k}{100}.$$

$$\therefore \text{increase in volume of unit vol. at } 0^{\circ}\text{C. for } 1^{\circ}\text{C. rise}$$

$$= \frac{(b - a) k}{a \times k \times 100} = \frac{(b - a)}{100 a}.$$

Express the result both in *vulgar* and in *decimal* fractions.

* The volume of the air in the tube = area of cross-section \times length. As the area of cross-section is the same at different parts of the tube, the volumes are proportional to the lengths as read off from the scale.

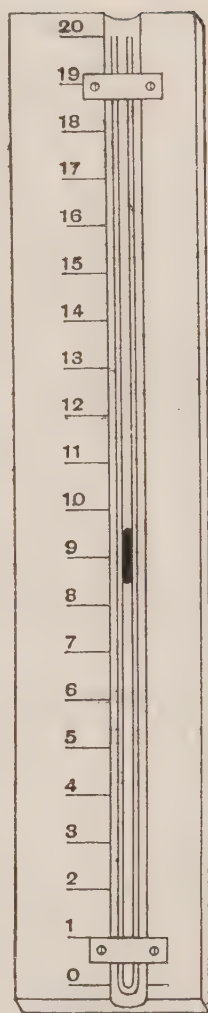


FIG. 21.

Charles's Law. Very accurate experiments on the expansion of air have shown that 1 c.c. at 0°C. becomes $1\frac{1}{273}$ c.c. at 1°C. The increase in volume gained by *unit* volume of air at 0°C. , when heated through 1°C. , is called the *coefficient of expansion* of air. The numerical value of the coefficient is $\frac{1}{273}$ or 0.00366.

It has also been found that *all* gases have the same coefficient of expansion, and this fact is comprised in the generalization (or general statement) known, usually, as **Charles's Law.** *The volume of a given mass of any gas at 0°C. increases by $\frac{1}{273}$ of this volume for every degree centigrade through which it is heated; conversely, the volume decreases by $\frac{1}{273}$ of its volume at 0°C. for every degree centigrade through which the gas is cooled, the pressure remaining constant.*

Suppose we have 273 c.c. of air at 0°C. On being heated from 0°C. to 1°C. its volume increases by $\frac{1}{273}$ of 273 c.c., i.e. by 1 c.c. 273 c.c. at 0°C. become $(273+1)$ c.c. at 1°C.

„ „ $(273+10)$ c.c. at 10°C.
 „ „ $(273+100)$ c.c. at 100°C.
 „ „ $(273+273)$ c.c. at 273°C.
 i.e. the volume is doubled at 273°C.

If cooled below 0°C. the volume decreases by $\frac{1}{273}$ of the volume at 0°C.

Thus 273 c.c. at 0° become $(273-1)$ c.c. at -1°C.
 „ „ $(273-10)$ c.c. at -10°C.
 „ „ $(273-273)$ c.c. at -273°C.
 i.e. the volume is reduced to 0 at -273°C.

The volume of a gas can never be reduced to zero, because before this temperature is reached the gas becomes a liquid or solid; in fact, Charles's Law does not apply at *very low* temperatures.

Since -273°C. is the temperature at which a gas should theoretically occupy no volume at all, it is sometimes called Absolute Zero or 0°A.

$$\text{Thus } 0^{\circ} \text{ A.} = -273^{\circ} \text{ C.}$$

$$10^{\circ} \text{ A.} = -263^{\circ} \text{ C.}$$

$$273^{\circ} \text{ A.} = 0^{\circ} \text{ C., \&c.,}$$

and the scale is called the Absolute Scale of temperature.

In calculating the influence of temperature on the volumes of gases it is convenient to make use of the absolute scale, and so avoid the necessity for first reducing the volume of a gas to 0° C.

Thus, to calculate the new volume after 15 c.c. of air at 10° C. have been heated to 20° C. :—

First change the C. degrees to A. degrees—

$$10^{\circ} \text{ C.} = (10 + 273)^{\circ} \text{ A.} = 283^{\circ} \text{ A.}$$

$$20^{\circ} \text{ C.} = (20 + 273)^{\circ} \text{ A.} = 293^{\circ} \text{ A.}$$

At 283° A. the volume is 15 c.c.

$$,, \quad 1^{\circ} \text{ A.} \quad ,, \quad ,, \quad \frac{15}{283} \text{ c.c.}$$

$$,, \quad 293^{\circ} \text{ A.} \quad ,, \quad ,, \quad \frac{15 \times 293}{283} \text{ c.c.}$$

Charles's Law may also be stated as follows :—

The volume of a given mass of any gas varies directly as its absolute temperature, provided that the pressure is constant.

If V is the volume of a gas when its absolute temperature is T , then if the absolute temperature is changed to T' , and V' represents the new volume, these quantities are related thus :—

$$\frac{V}{T} = \frac{V'}{T'}$$

This is the symbolical expression of Charles's Law.

Hence
$$V' = V \times \frac{T'}{T}$$

$$\text{or new vol.} = \text{old vol.} \times \frac{\text{new Abs. Temp.}}{\text{old Abs. Temp.}}$$

EXAMPLES V (a).

1. Express 15°C. , -15°C. , 0°C. , 273°C. , -273°C. in degrees absolute.
2. If some air occupies 117 c.c. at 17°C. , what space will it occupy at 0°C. ?
3. A gasometer of 6,000 cub. metres capacity is *half* filled with coal gas at 15°C. What volume will the gas occupy when the sun has raised its temperature to 20°C. ?
4. Some air at -10°C. is heated to $+10^{\circ}\text{C.}$, at which temperature it occupies 1 litre. What was the volume at -10°C. ?
5. Some air measured 75 c.c. at an unknown temperature, and 100 c.c. at 25°C. Calculate the original centigrade temperature.
6. Find the ratio of the volumes at 0°C. of gas *X* which occupies 220 c.c. at 27°C. to that of gas *Y* which occupies 440 c.c. at -23°C.
7. 5 litres of air are at 87°C. and 4 litres of coal-gas at -13°C. ; by how much will their volumes differ at 0°C. ?
8. Gas *A* had double the volume of gas *B* at 0°C. Calculate the temperature of *A* so that it shall have the same volume as *B* has at 182°C.
9. Which has the greater volume at 0°C. , 150 c.c. of coal-gas at 23°C. or 160 c.c. of air at 33°C. ?
10. One gas has three times the bulk of another when both are at 15°C. What will be the ratio of their volumes (a) at 0°C. , (b) at -15°C. ?

Exp. 2. To find the relation between the volume and pressure of a given mass of gas.

Required:—As in Fig. 22, mercury, pressure tubing, metre scale, tray.

DIRECTIONS. Set up the apparatus shown in Fig. 22, and place the whole on a tray. Clamp the glass tubes opposite one another. Pour in mercury through the funnel, and tilt *A* to let out some air, add more mercury if necessary, and by further tilting get the mercury about half-way up *A* (at B_1), and at the same time that in *D* must be at the same level, E_1 .

The mass of air we are going to experiment with occupies the space AB_1 .

Measure the perpendicular distances (in mm.) from A to C and from B_1 to C . Subtract and get the volume AB_1 and **record** it. Read the barometer in mm.

[When the level of the mercury in both limbs is the same, the air in A is at atmospheric pressure as given by the barometer.

If the mercury in D (as at E_2) is above that in A (B_2), the pressure of the enclosed air is found by adding the difference in level between E_2 and B_2 to the height of the barometer. When the level in D is below that in A as at E_3 , the pressure is height of barometer *minus* the difference in level between B_3 and E_3 .]

Raise D a little, measure E_2C and B_2C . Find new volume which is $AC - B_2C$ and new pressure which is Barom. ht. + $E_2C - B_2C$. **Record** these as below. Raise D a little more and get another set of results, and continue this until five volumes and pressures have been obtained.

Next, lower D so that the mercury level is below that in A , and get three or four sets of results. **Record** all these and multiply each volume by the corresponding pressure.

LABORATORY RECORD. Arrange results thus:—

Volume.	Pressure.	Vol. \times Pressure.
$AB_1 =$ mm.	Ht. of barom. = mm.	$\dots \times \dots =$
$AB_2 =$ „	„ + $E_2C - B_2C =$ „	$\dots \times \dots =$
$AB_3 =$ „	„ - $(B_3C - E_3C) =$ „	$\dots \times \dots =$
$\dots =$ „	„ - $\dots\dots\dots =$ „	$\dots \times \dots =$

Questions:—(i) What conclusion do you draw from the figures obtained by multiplication in the third column?

(ii) What are the chief experimental errors?

(iii) What will be the pressure when the original volume has been (a) halved, (b) doubled?

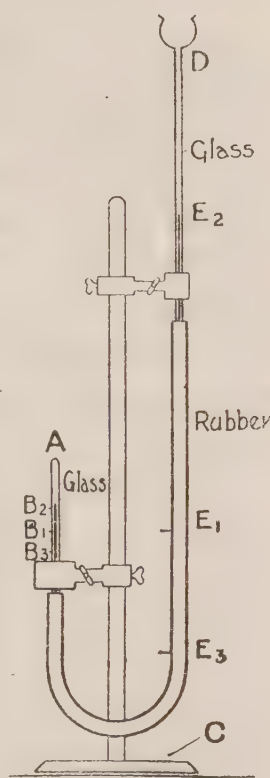


FIG. 22.

Boyle's Law. Exp. 1 shows that, for the same mass of air, the product obtained by multiplying the pressure by the volume is approximately constant. This is also expressed by saying that the volume is inversely proportional to the pressure.

These facts with regard to the effect of pressure on a given mass of air were first discovered by Robert Boyle in 1662. It has since been found that every other gas behaves, within certain limits, in a similar way. All these experimental facts are summed up in one general statement, called Boyle's Law, viz.: When the temperature is constant, the volume of a given mass of gas is inversely proportional to the pressure upon it.

The law may be conveniently expressed in symbols thus: Let P be the pressure, and V be the volume of a given mass of gas; if the pressure is altered to P' , the volume changes to, say, V' .

Then the law states that $PV = P'V'$. Suppose the volume V of a gas and its pressure P are known, and it is required to calculate the new volume V' resulting from the pressure changing to P' , which is also known.

$$\text{From above equation } V' = V \times \frac{P}{P'},$$

$$\text{or, new vol.} = \text{old vol.} \times \frac{\text{old press.}}{\text{new press.}}$$

The pressure of a column of mercury 760 mm. high is called the standard or normal pressure. It is approximately equal to the average pressure of the atmosphere at sea-level.

EXAMPLES V (b).

1. If 100 c.c. of air are under a pressure of 760 mm. of mercury, what will be the volume of the air at (a) 780 mm., (b) 740 mm.?

2. When the barometer stands at 75 cm. some air occupies 500 c.c. What *additional* pressure is needed to compress it to 400 c.c.?

3. What will be the difference in volume at 76 cm. pressure between a quantity of air *A* which occupies 5 l. at 74 cm. pressure, and another quantity *B* occupying 4 l. at 78 cm. pressure?

4. The pressure on some coal gas changes from 28 in. of mercury to 32 in. At the latter pressure the volume is 6 litres. What was its volume before the pressure changed?

5. At a pressure of 14 lb. per sq. in. some air occupies 15 cub. ft. What will be its volume under a pressure of (a) 12 lb. per sq. in., and (b) 16 lb. per sq. in.?

6. 20 c.c. of oxygen were compressed to 18 c.c. under a pressure of 760 mm. of mercury. What was the original pressure?

7. What decrease in volume of 1 litre of air at normal pressure will result from an increase of 20 mm. in the pressure?

8. At 76 cm. pressure the ratio of the volume of some oxygen to the volume of some nitrogen is as 2 : 1. What will be the ratio at (a) 70 cm., (b) 80 cm. pressure?

9. Gas *A* at 68 cm. pressure occupies three times the space of gas *B* at 85 cm. pressure. What is the ratio of the volumes at 76 cm. pressure?

10. Some air in an inverted cylinder standing over mercury measures 180 c.c. The level of mercury in the cylinder is 20 cm. above that in the trough. The barometer stands at 750 mm. Find (a) the pressure of the air, (b) the volume it would occupy if mercury was poured into the trough until the level was the same as that in the cylinder.

11. Find the pressure on the air in question 10 when water is substituted for mercury. (Sp. g. of mercury, 13.6.)

The alteration of the volume of a gas due to the simultaneous alteration of its temperature and pressure.

Suppose it is required to find the volume of a gas at 30°C . and 780 mm. pressure, knowing that at 15°C . and 770 mm. pressure it occupies 40 c.c.

The calculation may be done in two stages:

- (1) Find the change in volume due to change in temperature alone, the pressure being supposed to remain constant, and then
- (2) Find the alteration in volume due to change of pressure, the temperature being constant.

Thus (1) using the law of Charles—

Vol. at $(273+15)^{\circ}\text{A}$. and 770 mm. = 40 c.c.

$$\text{,, } 1^{\circ}\text{A. } \text{,, } \text{,,} = \frac{40}{(273+15)} \text{ c.c.}$$

$$\text{,, } (273+30)^{\circ}\text{A. } \text{,, } \text{,,} = \frac{40 \times (273+30)}{(273+15)} \text{ c.c.}$$

(2) Using the law of Boyle—

$$\text{Vol. at } (273+30)^{\circ}\text{A. and 1 mm.} = \frac{40 \times (273+30) \times 770}{(273+15)} \text{ c.c.}$$

$$\text{,, } \text{,, } \text{,, } 780 \text{ mm.} = \frac{40 \times (273+30) \times 770}{(273+15) \times 780} \text{ c.c.}$$

The symbolical expression for the laws of Charles and Boyle, using the same symbols as on pp. 63 and 66, is

$$\frac{VP}{T} = \frac{V'P'}{T'}; \text{ hence, } V' = V \times \frac{P}{P'} \times \frac{T'}{T}.$$

Knowing any five of these quantities we can find the sixth.

Before comparing the volumes of gases observed under different conditions of temperature and pressure one or both must be corrected, i.e. reduced to the volumes they would occupy if they were at the same temperature and pressure.

It is usual for purposes of comparison to reduce volumes to 'normal' or 'standard' conditions, i.e. 0°C . and 760 mm., often written as N.T.P. or S.T.P

For example, it is required to compare the volumes of two quantities of air, viz. :—

(a) 30 c.c. at 780 mm. and 15° C. with (b) 29 c.c. at 760 mm. and 10° C.

Both these volumes must be reduced to the same temperature and pressure ; for example, to S.T.P.

(a) 30 c.c. at 780 mm. and 15° C. become

$$\frac{30 \times 780 \times 273}{760 \times 288} \text{ at S.T.P.} = 29.18 \text{ c.c.}$$

(b) 29 c.c. at 760 mm. and 10° C. become

$$\frac{29 \times 760 \times 273}{760 \times 283} \text{ at S.T.P.} = 28.07 \text{ c.c.}$$

EXAMPLES V (c).

1. At 15° C. and 740 mm. pressure a gas occupies 85 c.c. What volume will it have at S.T.P. ?

2. Find the volume at 25° C. and 780 mm. pressure of a mass of gas occupying 15 litres at S.T.P.

3. What volume will 16 litres of air at -10° C. and 750 mm. pressure occupy at $+10^{\circ}$ C. and 770 mm. pressure ?

4. The temperature and pressure of a certain volume of air (measured at 20° C. and 700 mm.) change to 10° C. and 800 mm. when it has a volume of 65 cub. in. What was the original volume ?

5. A certain mass of gas occupies 18 c.c. at 25° C. At 50° C. and when the barometer stands at 29 in. its volume is 21 c.c. What was the original pressure in inches of mercury ?

6. What *alteration* in pressure would be necessary to change the volume of 3.5 cub. ft. of air at 7° C. and at a pressure of 14 lb. per sq. in. to 3 cub. ft. at 14° C. ?

7. Find whether (a) 18 c.c. of air at 740 mm. and 30° C., or (b) 18 c.c. of air at 750 mm. and 10° C., would occupy the greater volume at S.T.P.

Pressure of a gas partly filling an inverted tube. Gases are often collected in an inverted tube or jar which has previously been filled with mercury or water.

Suppose the gas has been collected over mercury and that it fills the tube, then its pressure is the same as that of the atmosphere and is ascertained by reading the barometer.

If, however, it does not entirely fill the tube, its pressure is less than that given by the barometer. In Fig. 23, if AB represents the volume of the gas, and BC is mercury, then, pressure of gas + pressure of BC = pressure of atmosphere,

\therefore pressure of gas = height of barometer — length of BC , both lengths being measured in the same units.

If BC contains water instead of mercury, the length BC must be divided by 13.6, because the pressure of a column of 13.6 cm. of water is equal to that of a column of mercury 1 cm. high.

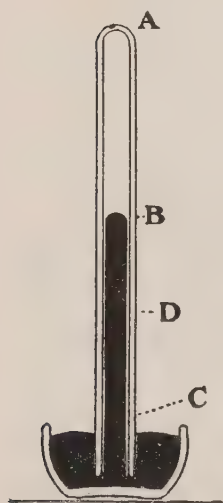


FIG. 23.

In this case the gas is damp, i. e. it is mixed with water vapour, and the pressure thus obtained is that of the mixture. The pressure of the dry gas is calculated as explained below.

Pressure due to each component of a mixture of gases. In Fig. 23 suppose the volume of AB is 40 c.c. and contains air, and suppose BC measures 30 cm. Then, if the barometer stands at 76 cm., we have 40 c.c. of air under a pressure of $(76 - 30) = 46$ cm. of mercury.

Now suppose coal-gas is introduced until the mercury falls to D . After a little time coal-gas will be found at every part of AD . Hence the volume of the coal-gas is that of AD , say 60 c.c., and the volume of the air is also 60 c.c.

What is the pressure of the air, and what is the pressure of the coal-gas?

The mercury in the trough will have risen a little, say to C . Suppose $DC = 10$ cm. Then we have

$$\begin{array}{rcl}
 \text{Pressure of} & \text{Pressure of} & \text{Pressure of} \\
 60 \text{ c.c. of air} & + & 60 \text{ c.c. of coal-gas} & = & (76 - 10) \text{ cm. of mercury.} \\
 & & & & = 66 \text{ cm. of mercury.}
 \end{array}$$

Since the pressure of the air was 46 cm. of mercury when its volume was 40 c.c., its pressure will be $46 \times \frac{40}{60}$ cm. = $30\frac{2}{3}$ cm. of mercury, since its volume has increased to 60 c.c. (Boyle's Law).

\therefore pressure of coal-gas is $(66 - 30\frac{2}{3}) = 35\frac{1}{3}$ cm. of mercury.

The *total pressure* of a mixture of gases is equal to the sum of the *partial pressures* of each component gas of the mixture.

This is known as Dalton's Law of Partial Pressures.

To calculate the partial pressure of each gas we must know the total pressure and also the volume of each component at some definite pressure. Thus, suppose we had 50 c.c. of a mixture of coal-gas and air standing over mercury in a tube, and that the height of the mercury in the tube was 10 cm. above that in the trough, and that the barometer stood at 76 cm.

\therefore we have 50 c.c. of the mixed gases at 66 cm. pressure.

If we are given that the air occupies $\frac{1}{5}$ of the volume of the coal-gas when both are measured separately at the same pressure, then the partial pressures are as follows:—

Partial pressure of air = $\frac{1}{5}$ of 66 = 13.2 cm.

„ „ coal-gas = $\frac{4}{5}$ of 66 = 52.8 cm.

To calculate the pressure of a dry gas from the pressure of the moist gas. Suppose we have 100 c.c. of air filling a jar inverted over water at a temperature of 15° C. Water vapour exerts at this temperature a pressure of 12.7 mm.* Suppose the barometer stands at 760 mm. Then the pressure of the air is $(760 - 12.7) = 747.3$ mm., hence its volume at 760 mm. would not be 100 c.c. but $100 \times \frac{747.3}{760}$ c.c. by Boyle's Law.

The pressure of the water vapour depends only on the temperature and not on the size of the vessel, provided that liquid water is present. The pressure of aqueous vapour is found from the table in the Appendix.

The vapour pressure of mercury at ordinary temperatures is so small that it is usually neglected.

* For the method of ascertaining the maximum vapour pressure of water at various temperatures books on Heat should be consulted.

Exp. 3. To find the weight of a litre of air at S.T.P.

Required:—Balance, 250 c.c. flask, &c., as in Fig. 24; measuring jar, beaker of water.

DIRECTIONS. Fit up the flask as shown in Fig. 24; see that the cork and tube fit tightly.

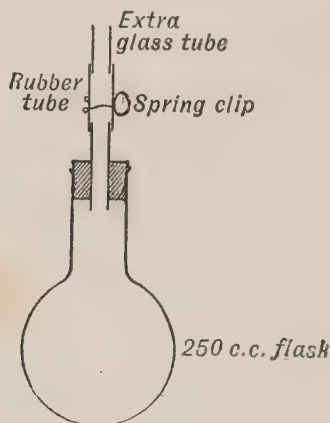


FIG. 24.

Weigh the flask with the tubes and clip in position. (Use the rider.)

Record the weight.

Temporarily connect a second glass tube to the rubber above the clip.

Through this tube suck out as much air as possible, holding the flask neck downwards. Close the clip before suction ceases.*

Precaution:—*Avoid letting saliva get into the permanent tubes or flask.*

Remove the extra glass tube, and weigh again, being careful to avoid draughts. **Record** the weight.

Invert the neck of the flask in water, and open the clip.

[Hold the flask by the neck—not the bulb.] **Note** what happens. Close the clip again, and place the flask upright.

Pour the water from the flask into a measuring jar.

Note the volume of water accurately. Read the barometer and take the temperature of the air.

LABORATORY RECORD. Diagram; record weighings thus:—

Weight of flask, &c., full of air . . . = g.

„ „ with some air withdrawn = g.

Weight of air withdrawn . . . = g.

Volume of water = volume of air withdrawn = c.c.

* If a Bunsen water-pump is available, air may be sucked from the flask by its use instead of by the method described above.

Calculate the weight of 1 litre of air (*a*) at the temperature and pressure of the room, (*b*) at S.T.P.

Questions :—(i) Why is it so necessary to avoid draughts when weighing?

(ii) Besides errors of weighing, what other errors are liable to be made? State whether they would make your result too large or too small. [The errors in this experiment are relatively large if care is not taken.]

(iii) What fraction of the total air in the flask were you able to draw out?

(iv) (*a*) How could you proceed to find the weight of *all* the air in the flask? (*b*) If you displaced the air in the flask by coal-gas and then weighed it, how could you find the weight of 1 litre of coal-gas without sucking out any of the gas?

(v) If a small rubber balloon were weighed (*a*) full of air, (*b*) without air inside, would any difference be observed? Give reasons.

(vi) Knowing that a solid weighs less in water than in air, do you think the weight in air would be different from the weight in a vacuum? Give reasons.

PROBLEM (V. 3). Find the weight of a litre of coal-gas by method suggested in question iv (*b*) above. [Be careful to avoid bringing the gas near a flame.]

Density of gases. When we know the weight of a given volume of a body, we can find its density by dividing its weight by the volume. *Density is the weight or mass of one unit of volume of the substance*, under the stated conditions of temperature and pressure. In the case of gases it is usual to take the litre as the volume unit, and 0°C. and 760 mm. as the temperature and pressure respectively. The densities of gases nearly all differ from one another, as do those of solids and liquids. The density of a gas is *very* much less than that of the same substance in the solid or liquid state and solids and liquids in general; e.g. 1 litre of water at 4°C. weighs 1000 g., 1 litre of air at 0°C. weighs 1.293 g. Thus water is nearly 800 times as dense as air.

To determine the *weight* of a gas evolved in an experiment

it is usual to observe its volume, temperature, and pressure, then to calculate its volume in litres at S.T.P., and finally to multiply this by the weight of 1 litre, i.e. by its density. It would be very laborious to weigh the gas directly, each time we wish to ascertain its mass.

EXAMPLES V (*d*).

1. The volume of some dry air standing in a graduated tube over mercury reads 50 c.c. The height of the mercury in the tube above that in the trough is 15 cm.; the barometer reading is 755 mm. What is the pressure of the air? What volume would it occupy at 760 mm. pressure?

2. 200 c.c. of air stand in an inverted cylinder over water at 10°C . The water level is the same inside and outside the cylinder. What is the pressure of the air? [Barometer reading is 753 mm.; pressure of aqueous vapour at 10°C . is 9.1 mm.]

3. 50 c.c. of air saturated with moisture at 15°C . stand over mercury as in question 1. Find the pressure of the dry air at 15°C . and its volume at 760 mm. of mercury pressure. (Pressure of water vapour at 15°C . = 12.7 mm. of mercury.)

4. 100 c.c. of dry air are measured at 20°C . and at 765 mm. pressure. If the air be now saturated with moisture, what volume will the damp air occupy, its pressure remaining 765 mm.? [The pressure of aqueous vapour at 20°C . is 17.4 mm.]

5. What weight of water vapour is contained in 1 cubic metre of air saturated at 20°C . and having a pressure of 753 mm.? [Pressure of aqueous vapour at 20°C . is 17.4 mm., and weight of 1 litre of aqueous vapour at 0°C . and 760 mm. is 0.8064 g.]

6. Calculate the weight of 1 litre of air at 15°C . and 750 mm., taking the weight at S.T.P. as 1.293 g.

7. What is the density of air at S.T.P. relative to that of water at 4°C .? Taking the relative density of mercury as 13.6, calculate the height of the atmosphere on the assumption that its density is uniform (1 l. of air at S.T.P. weighs 1.293 g.).

8. A litre of air at S.T.P. is heated to 125°C . and its density is found to have been halved; what alteration in pressure has it undergone?



CHAPTER VI

BURNING

THE first clear and definite ideas leading to the establishment of the modern science of Chemistry were obtained from the careful study of the phenomena of burning; from the knowledge thus gained the science developed rapidly in many directions.

The subject is familiar to everybody, but unless trouble has been taken to observe carefully and to reason accurately about these observations, only vague and perhaps erroneous impressions will have been formed.

In order to obtain a clear understanding of the subject, the first thing to do is to write down whatever is already personally known about it, care being taken to separate observations from mere opinions or explanations.

If in doing this any uncertainty is felt as to the accuracy of previous knowledge, it is plainly necessary to make fresh and careful observations on the doubtful points, allowing no preconceived notions to influence them. It is only in this way that facts can be ascertained. By the word *fact* is meant something which is beyond all doubt, something perfectly true and incapable of being altered. Hence the first step in the investigation of a subject is to *ascertain the facts* by means of careful observation.

Record of previous knowledge of burning. Make a list in your Fair Notebook of six or eight different substances you have seen burning, recording all the observations you can remember in a scheme thus :—

Name of substance.	Whether solid, liquid, or gas.	Whether there was a flame. If so, colour, &c.	What was left if anything after burning. Describe its appearance.	Any other observations.
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Then copy the following questions into the Fair Notebook and answer them, in order to classify the facts and to record the opinions you have formed. (*No help should be obtained and no books consulted.*)

Preliminary Questions.

1. Is burning *always* accompanied by a flame? Give examples.
2. Do all burning things vanish away, or is there something left behind? Or do some vanish and others leave a residue? Give examples.
3. In the case of any residue being left do you think it is lighter, heavier, or of the same weight as the substance before burning? Give a reason, or if in doubt, say so.
4. Do things start burning of themselves, or if not, how are they caused to burn?
5. (a) Can a substance be heated without burning?
(b) Can a substance be burnt without being heated?
Give examples, and explain the difference between 'heating' and 'burning'.
6. Is a match heated before it begins to burn? If so, how?
7. Why are paper and wood laid below the coal in a grate before lighting a fire?
8. Is it necessary to heat all things to the *same* temperature before they start burning? Compare matches with coal.
9. What difference is there between 'burning', 'smouldering', and 'scorching'?

10. Sometimes a fire does not burn well. How (without adding any more fuel of any sort) can a bright blaze be produced? How do you account for it?

11. Do you think that anything else besides fuel is necessary to keep the fire burning? Give a reason for your opinion.

Your answers to these questions will probably have shown that you already know several facts about burning, but that you are doubtful about others and, perhaps, unable to explain them all. The sensible and scientific way of clearing up the question is to begin with experiments on some simple case of burning, in the hope of being able to get a simple explanation. Afterwards, those cases which seem more difficult can be studied with a much better chance of success.

In order to carry out this plan we shall start with experiments on the burning of magnesium, a metal which is used in 'flash-light' photography.

Exp. 1. To observe what happens when magnesium burns.

Required:—10 cm. of magnesium ribbon ; porcelain dish ; tongs.

DIRECTIONS. Take a piece of magnesium ribbon about 10 cm. long and hold it with a pair of crucible-tongs in a flame.

Note what happens before it lights.

Hold the burning ribbon over a dish until it goes out.

Examine the residue, or ash (magnesia), and compare it with the magnesium by stating in each case whether—

- | | |
|--------------------------|-----------------------------|
| (a) it shines or not, | (b) it is brittle or tough, |
| (c) it will burn or not, | (d) it melts easily. |

LABORATORY RECORD. Observations in full.

Questions:—(i) Are the obvious properties of magnesium and of the ash the same or different?

(ii) Was all the ash collected, or did some escape?

(iii) Do you think the magnesium is contained in the ash or not?
If not, what has become of it?

(iv) Do you think the ash lighter, heavier, or of the same weight as the magnesium? Give a reason.

(v) Does the ash look like a single substance or a mixture?

Exp. 2. To find whether the ash weighs the same as the magnesium or not.

Required:—Porcelain crucible and lid (size 00) ; crucible-tongs ; pipe-clay triangle ; retort-stand and ring ; 15 cm. of magnesium ribbon, emery-paper, balance.

DIRECTIONS. *A.* Weigh a *clean* porcelain crucible with its lid.

Arrange it on a pipe-clay triangle resting on the ring of a retort-stand as in Fig. 25. Heat it for 5 min., and then allow it to cool ; reweigh when quite cold.

Record the weighings at once.

B. Bend 15 cm. of magnesium ribbon (previously brightened with emery-paper) and place it in the weighed crucible.

Weigh the crucible with its contents and the lid.

Arrange it as in Fig. 25 and put on the lid.

Heat with a small flame, so that the bottom of the crucible becomes red hot, and raise the lid from time to time.

When the burning appears to be finished, allow to cool with the lid on. Weigh again.

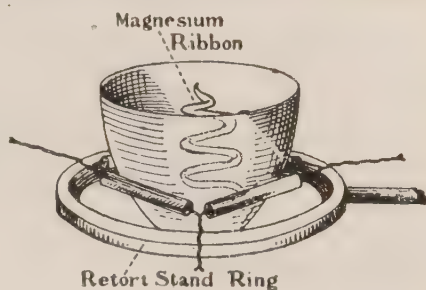


FIG. 25.

LABORATORY RECORD. Enter your weighings thus:—

Weight of crucible + lid + magnesium . . . = — g.

„ „ „ + lid . . . = — g.

∴ *weight of magnesium taken* . . . = — g.

Weight of crucible + ash + lid . . . = — g.

„ „ „ + lid . . . = — g.

∴ *weight of ash* . . . = — g.

Diagram of apparatus *actually used*, and *full* observations.

Questions:—(i) Is the weight of the ash different from that of the magnesium used?

(ii) Does the result confirm your previous opinion?

(iii) Did you notice any ash escaping? If so, how will this affect your result?

(iv) Why was the lid kept on most of the time?

Discussion of the fact discovered in Experiment 2.

The result of the weighings probably came as a surprise. If it did, it only shows how easy it is to form wrong opinions if trouble is not taken to perform experiments and to obtain correct observations.

It is now necessary to try to get an explanation of this fact. All the possible explanations should be thought of and further experiments devised to find out which one is most likely to be true.

There are four things present during the burning, viz. :—

- (i) The crucible ;
- (ii) The magnesium ;
- (iii) The air ;
- (iv) The flame.

The possible causes of the increase in weight are :—

- (1) The gas of the flame
 - (2) The air
- } might unite with the crucible.
- (3) The gas of the flame might possibly get into the crucible and unite with the magnesium.
 - (4) The air might unite with the magnesium.

Now Exp. 2, *A*, shows that a crucible heated in air by a flame does not alter in weight, therefore neither (1) nor (2) can be the cause.

To test (3) Exp. 2 must be performed again under similar conditions, but excluding the air.

PROBLEM (VL 2). Try to devise a method for testing the third explanation. Carry it out if approved ; otherwise do Exp. 3.

Exp. 3. To repeat Exp. 2, excluding the air.

*Required:—As in Exp. 2, with addition of some clean dry sand.**

DIRECTIONS. Put the magnesium at the bottom of the crucible and then fill it up with clean dry sand.

Weigh with lid on.

Heat, for about the same length of time as in Exp. 2, with the lid on. Allow to cool and reweigh.

Remove the sand and examine the residue.

Note whether it is magnesium or white ash.

LABORATORY RECORD. Observations and weighings.

Questions:—(i) What was the object of the sand?

(ii) Was there any alteration in weight?

(iii) Was the magnesium burnt or not?

(iv) Is the third explanation proved possible or otherwise?

(v) Do you think sand alters in weight on heating? If so, do

Problem 1 below.

PROBLEMS (VI. 3). 1. Find whether pure clean sand alters in weight on heating.

2. Using the same crucible repeat Exp. 2 very carefully, and calculate from your results how much ash can be obtained from 1 gram of magnesium.

3. Devise some way of showing plainly that air is used up when magnesium burns. If approved, carry it out.

* It is important that the sand should have been well washed and heated beforehand to free it from accidental impurities.

Hypothesis to account for the burning of magnesium.

The results of Exp. 3 will have shown that the third of the four possible explanations is incorrect. Therefore, unless some possible explanation was omitted from the list, it is right to conclude that the fourth one is correct.

This way of arriving at a conclusion is called the *method of exclusion*, because all the explanations but one have been excluded after an experimental test.

It is now possible to put forward, as a 'working hypothesis', the idea that the burning of magnesium consists in the union of the metal with air, and that the ash contains both magnesium and air.

The value of this hypothesis must now be tested by devising some further experiment, and predicting what ought to happen if the hypothesis is right.

(This shows one use of an hypothesis—it adds interest to experiments when they are performed with the object of finding whether a prediction is right or not.)

Suppose some magnesium is burned in a bell-jar which contains air, and which stands in a trough of water, the level of the water inside and outside being the same. (A bell-jar is open below and has a stopper on the top.)

Assuming the truth of the hypothesis, make *predictions*, on the following points, as to what ought to happen:—

- (i) If air is used up in burning, will the level of the water in the jar after the burning be lower or higher than it was before?
- (ii) Will the water rise or fall at the moment of putting the burning metal into the jar?

Submit these for inspection before proceeding.

*Exp. 4. To observe the combustion of magnesium in a confined volume of air.

Required:—Bell-jar with ground rim and cork to fit, glass trough as deep as possible, magnesium ribbon, glass rod, wire.

DIRECTIONS. Arrange a bell-jar as in Fig. 26 in a fairly deep trough. Twist one end of a loose coil of copper wire round a glass rod which passes through the cork, and put 4 or 5 pieces of magnesium ribbon within the coil, fixing them at the top.

Ignite the magnesium, place it in the mouth of the bell-jar quickly, and press in the cork tightly. **Note** what happens to the water in the bell-jar—(a) immediately after corking, (b) a few minutes later; also **note** whether the bell-jar becomes hot.

Pour water into the trough until the levels inside and outside the jar are the same, and remove the cork.

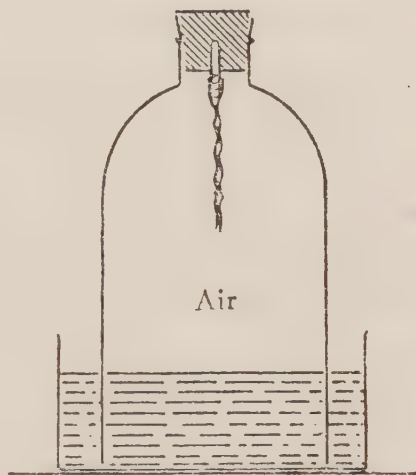


FIG. 26.

Quickly put a lighted taper into the jar.

Note what happens to the taper.

LABORATORY RECORD. Diagram and observations.

Questions:—(i) Was your second prediction (p. 82) correct?

Explain the behaviour of the water.

(ii) Was your first prediction correct?

(iii) Is the hypothesis confirmed or not?

(iv) Account for what happened to the taper.

(v) Was the gas left in the jar ordinary air or not?

* Demonstration.

Theory of the burning of magnesium. Exp. 4 has confirmed our 'working hypothesis' (p. 82), viz. that magnesium during burning unites with air, for the volume of air in the bell jar diminished considerably. The experiment has also shown that the residual air extinguishes a lighted taper, while ordinary air does not. Hence there appear to be two gases in ordinary air, one which supports the combustion of a taper and the other which does not.

The working hypothesis or theory must be tested by further experiments, which will either confirm it or cause it to be modified.

If our theory is true, then

$$\left. \begin{array}{l} \text{the weight of} \\ \text{ash formed} \end{array} \right\} = \left\{ \begin{array}{l} \text{weight of magnesium} \\ \text{burned} \end{array} \right\} + \left\{ \begin{array}{l} \text{weight of the} \\ \text{part of the} \\ \text{air used.} \end{array} \right\}$$

If an experiment can be arranged to settle this point, the theory will be established beyond a doubt.

What is required is to weigh (*a*) some air, (*b*) some magnesium, then (*c*) to burn the magnesium in this air without letting any escape, and finally to weigh (*d*) the ash and (*e*) the air left.

In order to prevent air escaping, a closed vessel must be used. Now air expands on heating, but if this is prevented it produces a pressure on the inside of the vessel which might be great enough to burst it.

Exp. 1, if carefully done, will have shown that the magnesium did not catch fire the moment it was put in the flame, but took several seconds, and had actually begun to melt.

Again, Exp. 4 showed that during the burning great heat is given out, causing the air to expand so much that some of it was nearly (or perhaps quite) driven out of the bell-jar.

From both these causes it seems impossible to carry out the proposed experiment, especially if the magnesium is heated in a closed flask or tube, as we should have first to heat the glass, which would soften and so make it easy for the air, which is trying to expand, to burst out.

It would not do to ignite the weighed metal as in Exp. 4 and then put it into the flask, because, however quickly it was done, some ash would be lost (as smoke) before the flask could be corked.

Here is a difficulty often encountered in experimental work, viz. the difficulty of carrying out a proposed experiment because a workable method cannot be devised.

If only the magnesium did not require so much heating *before* it started burning, it might be possible to get a flask or tube strong enough to stand the air-pressure caused by the heat given out *during* the burning.

In such a case, the only thing to do is to use some other substance which starts burning at a lower temperature.

It is first necessary, however, to be quite sure that this new substance, when it burns, behaves like magnesium, viz. :—

(1) that it forms an ash heavier than itself;

(2) that it uses up part of the air while burning.

If this is found to be so, then it will be fair to use it instead of magnesium for the final experiment.

Phosphorus, a substance used for making matches, is suitable for this purpose:

The burning of phosphorus. There are two varieties of phosphorus, the yellow and the red. The former catches fire at a temperature very little above that of the hand, so that it is necessary to be very careful in dealing with it.

Precaution :—*Phosphorus must never be touched with the fingers, and must be kept and cut under water.*

Exp. 5. To find whether phosphorus forms an ash when it burns.

Required:—Yellow phosphorus; porcelain tile; glass rod; dry wide jar or bottle, and glass plate to cover it; tongs; taper.

DIRECTIONS. *A.* Put a piece of dry yellow phosphorus, about the size of a pea, on a fragment of porcelain resting on a tile.

Touch the phosphorus with a warm glass rod, and as soon as it begins to burn, cover it with a *perfectly dry* inverted bottle or wide jar.

Note what happens and whether the bottle gets hot.

Allow it to stand for some time; meanwhile answer the questions below.

B. When cold, slip a glass plate under the mouth of the bottle, and place it right way up.

Precaution:—*If any phosphorus is left on the porcelain it may catch fire; if so, remove it to a draught cupboard, using tongs, and let it burn away.*

Remove the plate, and put a lighted taper into the bottle.

Note the result.

LABORATORY RECORD. Diagram; full observations in *A* and *B*.

Questions:—(i) Does burning phosphorus form an ash like magnesium?

(ii) Could Exp. 2 be repeated with phosphorus? Give a reason.

(iii) What is the smoke you saw?

(iv) Is the air left in the bottle (or jar) ordinary air?

(v) Do you think that air has been used up in the burning or not?

(vi) Why is yellow phosphorus kept and cut under water?

Exp. 6. To find what proportion of air is used up when phosphorus burns in it.

Required:—Bell-jar with rubber stopper through which a long glass rod passes, and as in Fig. 27; yellow phosphorus; taper.

DIRECTIONS. *A.* Place a piece of yellow phosphorus on a crucible-lid resting on a piece of wood, or cork, which floats on water in a trough.

Cover with the uncorked bell-jar.

Heat the lower end of the glass rod (not shown in Fig. 27) carrying the stopper; cork the bell-jar quickly and push down the hot rod till it touches and ignites the phosphorus. Then draw the rod up a little.

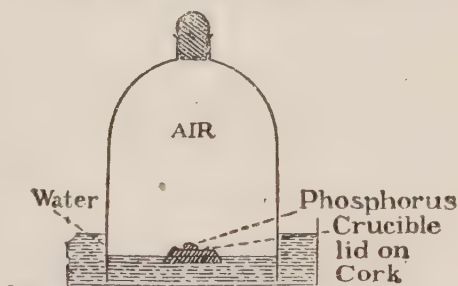


FIG. 27.

Note what happens to the level of the water—

(a) at first, (b) afterwards.

Allow the jar to cool while making your notes.

B. Estimate the amount of air used up.

C. Test the residual air with a lighted taper.

LABORATORY RECORD. Diagram; observations *A*, *B* and *C*.

Questions:—(i) Compare the effect on the water level with that of Exp. 4.

(ii) What has become of the ash a quarter of an hour after the burning? Did the same happen to magnesium ash?

(iii) How much air has been used up?

(iv) Was any phosphorus left unburnt? If so, why did it not go on burning in the air which remained?

(v) What conclusion can you draw respecting the nature of air?

N.B.—This experiment only *roughly* indicates the proportion of air used up. Exp. 6, p. 111, is a more accurate method.

Exp. 7. To find whether the ash is heavier than the phosphorus used to make it.

Required:—Light bulb-tube and dried asbestos arranged as in Fig. 28; aspirator, balance.

DIRECTIONS. Fit a bulb-tube with a cork and exit-tube as shown in Fig. 28, and find whether it is air-tight.

Introduce a small piece of dried phosphorus into the bulb and, using a glass rod for the purpose, pack the part *A* loosely with *recently dried* asbestos wool, leaving a space for the cork.

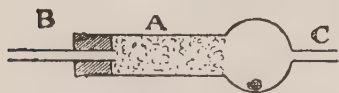


FIG. 28.

Blow gently through the tube to be sure that there is an air passage. (If not, the asbestos must be loosened.) Weigh the whole *quickly*.

Attach B to an aspirator and draw a *slow* current of air over the phosphorus. (If the phosphorus does not catch fire, warm it gently.) Allow it to cool and reweigh.

LABORATORY RECORD. Diagram, weighings, and observations.
Questions:—(i) What is the use of the plug of asbestos?

(ii) Is the ash heavier than the phosphorus?

(iii) Did any ash escape? If so, how does this affect the results?

(iv) Do you think it is as easy to work with phosphorus as with magnesium or not? Give a reason.

(v) Will the same theory account for the burning of phosphorus as for magnesium?

(vi) Will it be fair to use phosphorus to test our theory further?

Exp. 8. To find whether the weight of phosphorus-ash is equal to the weight of phosphorus burnt + weight of air used up.

Required :—300 c.c. flask shown in Fig. 29 ; sand, balance.

DIRECTIONS. Arrange the apparatus as shown in Fig. 29, without the phosphorus. See that the flask and sand are dry and cold, and that the cork fits tightly.

Introduce the phosphorus and fix the cork firmly in position. Weigh the whole *quickly*.

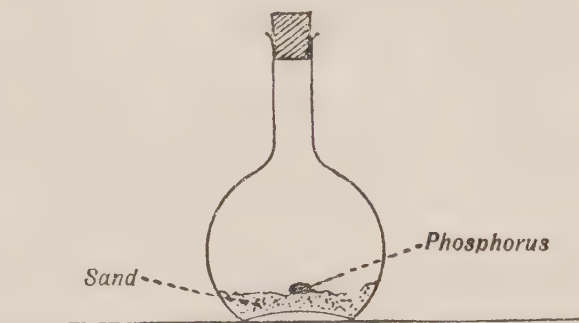


FIG. 29.

Hold the flask 6 inches above a *very small* flame, so as to warm the sand *carefully*. Stop heating as soon as the phosphorus melts (44°C.), and shake the sand round and round to start the burning. Allow the flask to cool and reweigh.

Remove the cork for an instant and then replace it. Weigh the whole a third time.

Precaution :—Do not empty the flask into the waste-box, but give it to the Laboratory assistant.

LABORATORY RECORD. Diagram and observations.

Wt. of app. + phosphorus + air, before burning = — g. (A)

Wt. of app. + unused phosphorus + unused air + ash = — g. (B)

Difference (if any) = — g.

Weight, after removing cork for a moment = — g. (C)

Questions :—(i) The total weight of apparatus, unused phosphorus and unused air was the same in both A and B, say x grams.

Is $A - x$, i. e. *weight of phosphorus and air used*, equal to $B - x$, the *weight of ash formed*?

(ii) Is the theory (p. 84) supported?

(iii) To what is the difference between B and C due?

Theory of the burning of magnesium and phosphorus.

If Exp. 8 has been carried out successfully, the theory (that the weight of the ash is equal to the sum of the weights of (*A*) the solid actually used up and (*B*) the part of the air used up) will have been found to be true, in the particular instance of phosphorus burning in air. Hence, in the case of phosphorus, we no longer call the above statement a *theory*, but a *fact*, since an experimental proof has been attained. It remains a theory for magnesium, and other substances, until it has been verified by experiment. The more verifications there are for particular cases, the more likely is the theory to be true in general.

From the length of time these experiments have taken, it is clear that years would be required to undertake similar experimental tests for all substances that burn. Since this is so, the results of other workers must be accepted, as long as there is no reason to doubt their accuracy. After a large number of substances have been thus tested, if no exceptions are found, it is usual to assume that the theory is true universally. It is then only necessary to attempt verification in cases which appear to present some obvious difference.

Whenever an ash heavier than the original solid is obtained, it may be taken for granted that the combustible behaves like phosphorus. Minor differences, such as temperature of ignition, amount of light emitted, physical properties of the ash, are to be expected, but these do not affect the theory. Exp. 9 will be made in order to note some of these differences.

Exp. 9. To find the effect of heating certain metals* in air.

Required:—Lead-foil; tin-foil; zinc-foil; copper turnings, free from oil; iron filings; crucible and lid; knitting-needle; balance.

DIRECTIONS. *A.* Cover the bottom of a small crucible with bits of the metal. Weigh the crucible, metal, and steel knitting-needle altogether.

B. Heat the crucible as in Exp. 2, stirring with the needle.

Precaution:—*Be careful not to lose any material from the stirrer.*

Note any change of colour, whether the metal melts, &c.

Continue to heat, and gently blow air on to the metal through a glass tube until a good deal of ash has formed.

Cool and reweigh.

LABORATORY RECORD. Weighings and observations for each metal.

Questions:—(i) Name the metals giving ashes heavier than the metal used.

(ii) State the colour and any peculiarity of the ashes.

(iii) Was a flame produced? If so, in which cases?

(iv) Can a substance be said to burn without giving a flame?

(v) Do these metals form an ash as quickly as magnesium?

(vi) What point have all these metals in common with magnesium and phosphorus, when heated in air?

Quick and slow combustion. It will now be perceived that the characteristic property of burning solids, so far as the experiments have gone, is the formation of a new substance (the ash) which is heavier than the original solid. If this ash is formed quickly there is generally a flame, but if slowly there is none. The former are cases of rapid burning or combustion (Latin, *comburo*, to burn up), and the latter, where there is no flame, of slow combustion. Such differences as the temperature at which burning (ignition) begins, the amount

* These metals should be distributed to different members of the class.

of heat given out during burning, the colour and other properties of the ash are minor differences, and must not prevent us from perceiving the general similarity of the action in all the cases.

QUESTIONS ON CHAPTER VI.

N.B.—*Refer to the note before the questions on p. 10.*

1. Write a revised set of answers to the preliminary questions (p. 76), recording them in your Fair Notebook after Exp. 9.
2. Describe the burning of magnesium and phosphorus in air, pointing out both the similarities and the dissimilarities.
3. Would you classify 'smoke' as a solid, liquid, or gas? Give reasons and examples.
4. Describe carefully how you would find the weight of magnesium contained in 100 grams of its ash.
5. Give a *concise* account of the reasons for concluding that magnesium-ash contains something from the air.
6. In the manufacture of bricks, the clay, after being cut into the proper shape, is 'burnt'. Is this a correct description of the change which takes place? Give reasons.
7. What is a *fact*? How are facts ascertained in chemistry? Give two examples.
8. What is a *working hypothesis*? What is a *theory*? Give examples from your work in this chapter. What is the use of a theory?
9. Discuss the question: Is air a single substance?
10. Describe *fully* an experiment to show that when phosphorus burns in air there is no loss of matter.
11. Compare the effects of heating lead and magnesium in air.
12. Give a *concise* account (without details) of the reasons for concluding that the combustion of phosphorus in air consists of the union of the phosphorus with a portion of the air.
13. When dry yellow phosphorus is allowed to stand in air it fumes and is said to smoulder. Account for this.
14. Why is yellow phosphorus usually kept under water? Would other liquids do instead? Why is it unadvisable to handle dry phosphorus?

CHAPTER VII

LAVOISIER'S WORK ON COMBUSTION

THE experiments of Chap. VI have shown that, in the case of the substances considered, *combustion in air consists in their union with a portion of the air to form an ash*. The following question now arises: Is it possible to get back from an ash—

- (A) the original solid,
- (B) the portion of the air it contains?

Preliminary Questions.*

1. What experiments can you suggest to try to solve the above question?
2. If your method succeeded, would the theory (p. 90) lead you to expect the total weight of *A* and *B* to be equal to that of the ash or not?
3. Would you expect *B* to let things burn in it? If so, would the whole or only a portion of the gas *B* be used up if enough metal were present?
4. Do you think burning would go on quicker, or at the same rate, in *B* as in air?
5. If you could get back the air used in Exp. 6 (p. 87) and mixed it with what was unused, would you expect the mixture to be the same as the original air or not?

* To be copied out and answered in the Fair Notebook like those on p. 76.

Historical note on combustion. Previous to the year 1774, the distinguished French chemist Lavoisier had been engaged in making experiments somewhat similar to those in Chap. VI and had arrived at the same theory. He used many metals, and also sulphur, charcoal, &c., but not magnesium, as it was then unknown.

He thought it would afford a splendid confirmation of his theory if he could get back from an ash (or calx as he called it) both the metal and the part of the air used up in burning. First he tried the effect of heating different calces, or ashes, to a very high temperature, but met with no success until 1774, when Dr. Priestley informed* him that when the solid calx of mercury was heated, it yielded liquid mercury and a gas having very remarkable properties. This hint was just what Lavoisier needed. Before seeing Priestley, he had been unable to make any ash give back the substances he knew it to contain. He was in a position similar to that which arose in Chap. VI, when it was found that experimental difficulties interfered with the practicability of the proposed experiment with magnesium (p. 84). Just as it was considered fair then to use phosphorus instead of magnesium, so Lavoisier thought that if he could get an experimental proof of his theory in the case of mercury-ash, it would turn theory into fact in this particular case, and would serve as a strong confirmation of the theory for the large number of other cases.

* The date of this discovery, August 1, 1774, is sometimes regarded as the birthday of modern chemistry; *v.* No. 7, Alembic Club Reprints (published by Simpkin, Marshall & Co.).

Exp. 1. To find the effect of heating calx of mercury.

Required:—Ignition tube ; wood splinters ; balance.

DIRECTIONS. Place a *little* of the powder in an ignition tube. Weigh it. Wrap a strip of paper round the mouth of the tube to hold it by, and heat the closed end in a Bunsen flame. **Note** the change in colour and any other effects. Light a wooden splinter, blow out the flame so as to leave the end glowing, and put it in the mouth of the tube. **Note** what happens and repeat two or three times. When the glowing splinter is no longer relighted, remove the tube from the flame and watch it while cooling. Reweigh when cold.

Rub the mirror on the side of the tube with a spill of filter-paper and shake out the contents of the tube into a basin. **Note** and identify the new substance.

LABORATORY RECORD. Description and observations.

Questions:—(i) Has the heating resulted in altering the weight of the contents of the tube?

(ii) Does the gas support the combustion of wood as well or better than air? (See question 4, p. 93.)

(iii) How could you collect a little of this gas?

(iv) How would you find whether it dissolves in water?

(v) Suggest a method for collecting a larger quantity of the gas, assuming it to be insoluble in water. Draw a diagram.

PROBLEM (VII. 1). Devise a method for determining the weight of mercury in 100 g. of the *dry* powder. Carry it out, if approved.

Priestley called this new gas 'vital air', but Lavoisier re-named it **oxygen**. The red powder was also named 'oxide of mercury'.

The term **analysis** or **decomposition** is applied to any process whereby two or more different substances are obtained from a single substance, without the intervention of a second substance.

Exp. 2. To collect oxygen from mercury oxide, and to burn substances in it. (*Priestley's experiment.*)

Required:—Dry mercury oxide, hard-glass tube, &c., as in Fig. 30; small gas-jars, cover-plates, magnesium, phosphorus, deflagrating spoon, knitting-needle.

DIRECTIONS. Arrange the apparatus as shown in Fig. 30, and see that the cork is air-tight.

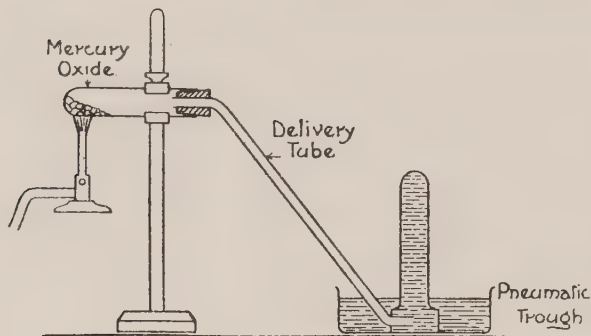


FIG. 30.

Fill a small test-tube and two gas-jars with water and let them stand inverted in the trough.

Heat gently at first, moving the flame backwards and forwards along the tube. Collect the first bubbles of gas in a *small* test-tube.* When it is full, close the mouth with your thumb, and put in a glowing splinter. **Note** whether it is oxygen or merely air.

Precaution:—*Do not remove the flame without first disconnecting the delivery-tube.*

When you have found that the oxygen is coming off, fill two jars with the gas, leaving them inverted in the trough.

Remove the delivery-tube from the trough, withdraw the lamp, and allow the tube to cool. Transfer a jar of the gas to the bench, using a cover-plate. Hold a strip of magnesium ribbon with tongs, ignite it and place it in the jar. **Note** the effect, and compare the ash with that obtained by burning the metal in air.

Put a little red phosphorus in a deflagrating spoon, ignite

* This method of collecting gases by displacement of water was invented by Priestley, and is still used for gases which do not dissolve much in water. The trough was called a 'pneumatic' trough, *pneuma* being the Greek for air or gas.

by touching it with a hot wire, and place it in another jar of the gas. **Note** the effect and the brilliancy of the flame.

Precaution :—*Burn off the residual phosphorus in a draught cupboard ; do not put it in the waste-box.*

LABORATORY RECORD. Diagram ; full observations.

Questions :—(i) What is the reason for the first precaution ?

(ii) Is the solid, left after magnesium has burned in oxygen, the same as that obtained when air was used or not ? State the evidence.

(iii) Is oxygen appreciably soluble in tap-water ?

Lavoisier's Experiments. When Lavoisier had verified Priestley's discovery of oxygen he proceeded to test his theory by two experiments.

In the *first experiment* his object was to heat the mercury in a known volume of air, and to observe :—

(a) the weight of mercury used up ;

(b) the volume of air " "

(c) the weight of the calx formed.

In the *second experiment* the object was to heat the calx obtained and to observe (d) the volume of gas, (e) the weight of mercury obtained.

The first may be described as the quantitative synthesis of the red oxide of mercury.

Synthesis or combination is the name given to the process by which a single substance (in this case the red oxide) is obtained by the union of two or more different substances (in this case the mercury and the oxygen from the air).

The second experiment is the quantitative analysis of the calx.

Lavoisier's synthesis of the red oxide of mercury. Fig. 31 shows apparatus with which the experiment can be imitated. In order to obtain a fair quantity of the red oxide a large volume of air has to be used, and this has to be heated to over 300°C . with pure mercury. It would be impossible to heat such a large volume of air in a closed glass vessel without great danger of bursting. Hence Lavoisier designed to heat the mercury with only a small quantity of air at once, viz. that in F, the bulk of the air remaining cold in A. The mercury in the trough B and for a short way up A prevents the escape of air, but yields a little when F is heated, as the expansion of the air there causes an increase of pressure.

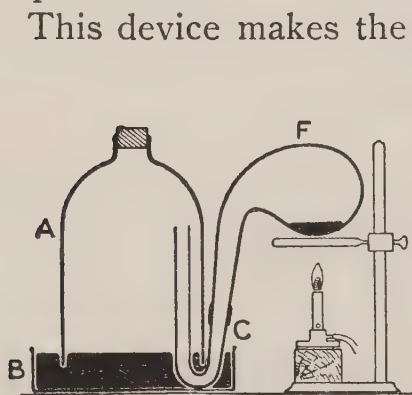


FIG. 31.

This device makes the experiment a slow one, for all the air in A has to diffuse through the tube C into F, and this takes much time. The tube C goes high up into A, because heating has to be stopped from time to time to find out when the action has finished. Then the mercury from the trough rises in A, and the end of C must be above this level, otherwise mercury from the trough would get into C and so block the passage between A and F.

The internal capacity of the whole apparatus F, C, and A, is found by filling with liquid and pouring it into a measuring vessel. Then a small weighed quantity of mercury is put into the retort F, and the vessel A placed in position. Heating was continued by Lavoisier for 10 days, red specks forming on the mercury in F, and on cooling the level to which the mercury rose in A was marked. After heating for 2 days longer and cooling again, the mercury rose no further in A than before. Hence it was concluded that the action had finished.

The volume of air which had disappeared was measured ; the red powder was separated from the residual mercury in F and both weighed.

Lavoisier's analysis of red oxide of mercury. The *object* of this experiment was to heat all the red powder previously obtained and to observe (a) the weight of mercury recovered, (b) the volume of oxygen recovered. Fig. 32 shows apparatus for carrying this out. The weighed red powder is placed in a hard-glass tube connected with a delivery-tube which terminates near the top of the receiving vessel. The latter is nearly full of mercury to begin with, its exact level being known.

The powder is heated until no more remains. On cooling the volume of gas in the receiver is ascertained and the mercury remaining in the hard tube is weighed.

Lavoisier found that he recovered approximately the same volume of gas and the same weight of mercury as disappeared in the first experiment.

Thus Lavoisier demonstrated the truth of his theory of combustion, viz. when a substance burns in air the calx (or other product) contains the original substance united to oxygen from the air, and also that during combustion no matter is lost, for when the change can be reversed, both the original substance and the oxygen are recovered intact.

Historical importance of Lavoisier's experiments with mercury. Several experiments on the effect of heating metals in air had been performed long before Lavoisier's time.

Another Frenchman, Jean Rey,* found, about the year 1630, that the calces of tin and lead were heavier than the metals before heating. He rightly concluded that the increase was due to the weight of air added, but unfortunately

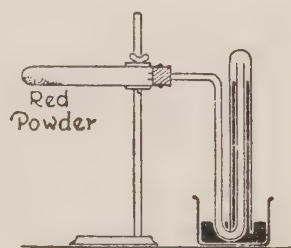


FIG. 32.

* Alembic Club Reprints, No. 11.

his work did not attract much attention, especially as it was opposed to the prevailing idea that substances were lighter after burning than before.

In those days, most educated people considered it undignified to make experiments: they thought that true knowledge could be obtained merely by discussions and arguments about casual observations. They chiefly devoted themselves to imaginary theories which had no proper experimental foundation, and became so prejudiced, that they either denied such facts as Rey had observed, or invented fanciful theories to account for them. At this time books were expensive and scarce, so that Rey's discoveries and explanations were soon forgotten.

A little later in the same century, three distinguished investigators working at Oxford, Robert Boyle (1625-1691), Robert Hooke* (1635-1703), and John Mayow (1645-1679), also proved by their experiments that air is used up when substances burn, and Mayow arrived at the same explanation as Rey. Unfortunately their work shared the same fate as Rey's and for the same reasons.

Another worker in the same field was the Swedish chemist Scheele† (1742-1786), who also proved that air was partly used up during burning. A great many of the experiments of these pioneers of modern science are very interesting; none of them, however, had managed to find out so much about air as Lavoisier (with Priestley's help) had done, and as some of them had not shaken themselves free from the prejudices of the current fanciful theories, they did not always draw correct conclusions from their facts.

It was Lavoisier who first thoroughly freed himself from the trammels of these prejudices, and trusting entirely to the facts he observed, framed his hypothesis of burning on them alone. This is the only method—and it cannot be repeated too often—by which true scientific knowledge can advance,

* Alembic Club Reprints, No. 5.

† Ibid., No. 8.

viz. by an unprejudiced explanation of carefully observed facts.

Not only was Lavoisier distinguished by his logical conclusions and hypotheses, but also by the trouble he took to really get at the facts by his constant use of the balance. A famous Scotch man of science, Black (1728-1799), had done a great deal to insist on the necessity of this in all chemical work, and Lavoisier appreciated his arguments to the full. You will probably have seen, in the early experiments of Chap. VI, how many of your previous ideas of burning were proved to be wrong when submitted to the test of the balance, and how important its use is.

This extract from the history of chemistry shows how the progress of the true knowledge of burning was delayed for 150 years (i. e. from the time of Rey to that of Lavoisier) by neglecting to carry out the principles of true scientific method mentioned above.

The indestructibility of matter. In Exp. 8 (p. 89) it was found that the weight of the phosphorus-ash was equal to the total weight of the phosphorus and air used up. Again, Lavoisier's experiments show that neither mercury nor air is lost during the formation of the calx. The latter contains exactly the amount of mercury and of air used up. Hundreds of similar experiments have been made, and they all show that **the total weight of the substances which take part in a chemical action is equal to the total weight of the new substances produced.** Consequently the theory has been put forward that *matter cannot be destroyed*, any more than it can be created. All that experiment can do is to rearrange the matter of substances in different combinations, as, for example, when some of the matter of air was taken away and combined with the matter of mercury; this rearranged matter constitutes the red calx of mercury. This seems very simple and plain after working with the balance, but in former times the theory did not meet with general acceptance. For instance, when a

candle burned it seemed to produce nothing. It was thought that the matter of the candle was utterly lost—that the weight of the earth was less after the burning than before, by the weight of the candle.

This theory or *Principle of the Indestructibility of Matter*, as it is called, is the foundation stone of experimental chemistry. All experiments and theories depend on it, and it is accepted by every one because no contradictory facts are known.

So firmly is this principle or theory established that it is sometimes referred to as the *Law of Conservation of Mass*.* The word 'law' indicates that the statement is known to be a fact in a very large number of cases, and, there being no known exceptions, it is assumed to be true in *all* cases.

QUESTIONS ON CHAPTER VII.

1. Who discovered oxygen, and on what date? What bearing had this discovery on the development of the theory of burning?

2. What is a pneumatic trough? What use is it put to in chemistry?

3. Describe a method for preparing oxygen from red mercury oxide. How may oxygen be distinguished from air?

4. Give a detailed account of the combustion of wood, magnesium, and phosphorus in oxygen, comparing them with similar combustions in air.

5. Define and give examples of the terms *synthesis* and *analysis*.

6. Draw up a concise account of Lavoisier's experiments with mercury oxide, showing clearly how they afford

(a) a confirmation of his theory of combustion;

(b) a verification of the principle of the indestructibility of matter.

7. State the Law of Conservation of Mass, and show how it can be verified in the case of phosphorus burning in air.

8. Explain, as clearly as you can, the methods of investigation adopted by Lavoisier which enabled him to achieve success where others had failed.

* The word 'conservation' means the same as 'preservation', and by 'mass' is meant 'weight as found by a balance'.

CHAPTER VIII

THE GASES OF THE AIR

The two principal gases in air. It has been observed (p. 87) that only a small portion of air is used up by burning phosphorus: the larger portion remains unaffected. By the use of mercury, Lavoisier was able to separate air into these two distinct parts. He found, on mixing them again, that the mixture had all the properties of ordinary air. Thus the fact was established that air consists of a small active part (oxygen) and a large inactive part, called *nitrogen*.

Lavoisier's nomenclature. To the ash of a metal he gave the name **oxide**, instead of calx, and to the process by which the oxide was formed, **oxidation**, instead of **calcination**. The latter term is, however, still occasionally used.

The following list of some of the oxides which have been made shows both the old and new names:—

<i>Old Names.</i>	<i>New Names.</i>
Red precipitate or calx of mercury.	Oxide of mercury or mercury oxide.
Litharge " " lead.	" " lead " lead "
Magnesia " " magne- sium.	" " magne- sium " magnesium "
Zinc white " " zinc.	" " zinc " zinc "
Calces of tin and copper.	Oxides of tin and copper.

Similarly, the white powder produced by burning phosphorus in air is called oxide of phosphorus.

After Priestley's discovery of oxygen it was found that the gas could be obtained from many other substances, some natural, some artificial, but all less costly than oxide of mercury.

Exp. 1. To observe the action of heat on nitre, red lead, potassium chlorate, and manganese dioxide.

Required:—As above; ignition tubes (one hard), splinters.

DIRECTIONS. Heat, in an ignition tube, about 1 g. of each substance separately, and finally a mixture of potassium chlorate (2 g.) with a smaller quantity of manganese dioxide. Use a hard ignition tube for heating manganese dioxide alone.

Note the effect of heat in each case, and test continually for oxygen.

Continue heating until no more gas is given off, and roughly estimate which gives the largest yield.

Note whether the substance melts; whether much or little heat is required; the nature of the residue.

LABORATORY RECORD. Enter observations thus:—

Name of substance.	Does it melt?	Is much heat required?	Is much oxygen produced?	Nature of the residue.

Questions:—(i) Which substance seems to yield most oxygen?

(ii) Which yields the oxygen without melting?

(iii) " " " " at the lowest temperature?

(iv) Hence, which method would be most convenient for obtaining large quantities of the gas?

(v) Draw a diagram of the apparatus you suggest for (iv).

PROBLEMS (VIII. 1). 1. Find the percentage weight of oxygen obtainable from potassium chlorate. (Submit your scheme for approval.)

2. Heat a little (0.5 g.) of potassium chlorate strongly until it ceases to give off oxygen. Cool it and shake the residue with a few drops of warm water to form a saturated solution of this residual solid. Put a drop of this on a slip of glass, put a cover-glass over it, and observe its crystalline form under a microscope. Treat some of the unheated chlorate in the same way, and compare the results. The first substance is called potassium chloride.

Exp. 2. To prepare oxygen (usual laboratory method).

Required:—Potassium chlorate, manganese dioxide, small flask as in Fig. 33; 3 gas-jars, cover-plates, test-tube, deflagrating spoon, taper, charcoal, sulphur, wire gauze, lime-water.

DIRECTIONS. *A.* Fit up the apparatus as in Fig. 33, or what you suggested in question (v), p. 104. See that it is air-tight.

Fill one-third of the flask with a mixture of potassium chlorate and about a quarter of its bulk of manganese dioxide.

Place the flask over gauze, heat gently, and, after a short time, collect some of the gas over water in a test-tube.

Test for oxygen. Then collect three jars full of the gas.

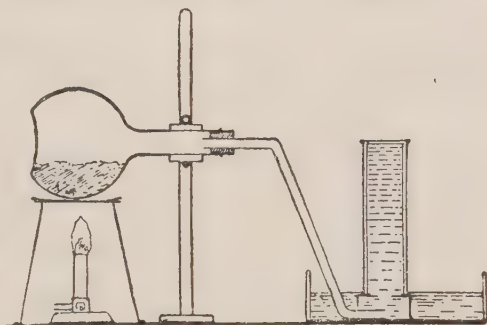


FIG. 33.

Precaution:—*Remove the delivery-tube from the trough before taking away the flame.*

B. Heat a piece of wood-charcoal on a deflagrating spoon, and then hold it in the air. **Note** whether it glows. Blow on it and **note** again.

Reheat and quickly put it in a jar of oxygen, so that the charcoal is about the middle of the jar when the mouth is closed by the disk. **Note** the effect, and leave till the charcoal has ceased to glow.

Withdraw the spoon and cover the jar with a glass plate.

Note the appearance of the charcoal.

Put (a) a lighted taper, (b) a little clear lime-water into the jar. **Note** what happens in each case.

C. Repeat *B*, using sulphur.

Note the effect of (a) heating it, (b) exposing it to air when hot, (c) placing it in oxygen, (d) putting a lighted taper

in the jar afterwards, and note (*e*) the smell of the gas in the jar, (*f*) whether the gas is soluble in water, by inverting the covered jar in a basin of water and shaking gently.

D. Put a little sand in the third jar of oxygen and repeat *B*, using a piece of iron gauze fastened to the spoon.

Before putting it into oxygen, dip it while red-hot into a little sulphur, which will burn and heat the iron while in the oxygen. **Note** whether the iron burns.

Collect and examine the solid which falls into the sand.

LABORATORY RECORD. Diagram of apparatus *used*; observations.

Questions :—(i) Why is the *round* part of the flask heated and not the base?

(ii) Why are the first bubbles not collected?

(iii) Give a reason for the precaution (p. 105).

(iv) Compare the effects of heating charcoal, sulphur, and iron in air with those observed on heating them in oxygen.

(v) What is the 'physical state' of the products obtained when these substances burn in oxygen? What names would you suggest for them, and how could you recognize them?

(vi) Has the manganese dioxide altered in appearance?

(vii) What is the colour of the residue left after manganese dioxide has been heated alone?

PROBLEM (VIII. 2). Devise a direct method for showing that sulphur uses up oxygen when it burns. Carry it out, if approved.

[*Revision Note*.—The oxygen thus prepared is liable to contain traces of chlorine (from the chlorate) and of carbon dioxide (from carbon mixed with the dioxide). Both are removed by bubbling the gas through a solution of caustic potash. The gas can be dried by passing it through concentrated sulphuric acid.]

Exp. 3. To find whether any oxygen is evolved from the manganese dioxide in Exp. 2.

Required :—Pure dried manganese dioxide, crucible, lid, potassium chlorate, balance, filter.

DIRECTIONS. Weigh a crucible, add about 3 g. of pure dry manganese dioxide, and weigh again. **Record** exact weight. Add powdered potassium chlorate to half fill the crucible, stir

the mixture with a dry rod (losing none), arrange on a tripod, partly covering the crucible with a lid, and heat for 5 min., during which time a good deal of oxygen will have escaped.

Cool and separate the insoluble black powder from the soluble white powder, as in Exp. 5, p. 36. The filtrate need not be kept, but *all* the black solid must be collected on a previously weighed filter-paper, dried, and weighed.

LABORATORY RECORD. Weighings and observations.

Questions:—(i) Has the weight of the black powder appreciably altered?

(ii) Has it changed in appearance?

(iii) Does it lose oxygen when heated with the chlorate for a short time?

(iv) Would it lose oxygen if heated with the chlorate until no more oxygen could be obtained?

Catalysis. Exp. 2 introduces a peculiar kind of chemical action called **catalysis**. Exp. 3 showed that the manganese dioxide remains unchanged at the end of the action, yet it undoubtedly causes the potassium chlorate to part with its oxygen at a lower temperature and at a greater rate than is the case when the chlorate is heated alone. A substance which appears to aid a chemical action without suffering alteration itself is called a **catalytic agent**, e.g. the manganese dioxide here acts as such an agent. Other examples will be noted later.

Exp. 4. To find the weight of a litre of oxygen.

Required:—*Small hard-glass tube, dried asbestos, potassium chlorate, and as in Fig. 34.*

DIRECTIONS. Fix up the apparatus as in Fig. 34, using a good rubber stopper for the flask. See that all is air-tight. The flask should hold at least 400 c.c. and the jar 300 c.c. The tube connecting the two should almost touch the bottom of the flask, and the limb entering the jar should descend to the same level.

Fill the flask with water, remove A, open the clip, and fill

the connecting tube with water by blowing. Fix the clip and pour out any water which has entered the jar.

Put a *little* powdered potassium chlorate and then a loose plug of *dried* asbestos wool into A, and weigh, using the rider. **Record** weight. Put A in position, open the clip, and heat the chlorate gently at first and then more strongly.

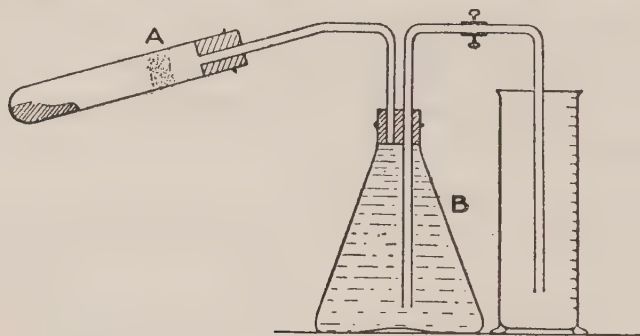


FIG. 34.

Stop heating when the jar is nearly full of water, and allow the whole to cool, the clip remaining open. Shake the flask gently to cool the oxygen, and after 10 min. cooling should be complete. When no more water is drawn from the jar to the flask, close the clip. Remove A and weigh carefully. Measure the volume of water in the jar, take the temperature of the water in the flask, and read the barometer.

LABORATORY RECORD. Diagram of actual apparatus. Enter results thus:—

Wt. of A + chlorate before heating = — g.

Wt. of A + residue after heating = — g.

Wt. of oxygen evolved = — g.

Vol. of water in jar after cooling = — c.c.

Temperature = —° C. Pressure = — mm.

Calculate the volume of dry oxygen at S.T.P. (p. 71), and then calculate the weight of 1 litre of oxygen at S.T.P.

Questions:—(i) Why was the tube dipping into the jar first filled with water?

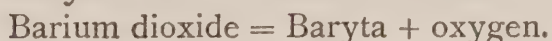
(ii) Why was it necessary to wait until everything was cold before measuring the volume of water in the jar?

(iii) Was the whole of the gas which entered the flask oxygen?

(iv) Is oxygen denser or less dense than air? [1 litre of air at S.T.P. weighs 1.293 g.]

Extraction of oxygen from the air. It is easy to obtain nitrogen from air because oxygen combines with many substances (phosphorus, sulphur, copper, &c.), which will not combine with nitrogen. On the other hand, there are no available substances which combine with nitrogen and which do not combine with oxygen.

It is therefore necessary to find whether there are any substances, like mercury (but cheaper and quicker in their action), which combine with oxygen and which give it up again on more intense heating. Several experiments have been tried, but none gave satisfactory results until Boussingault found that baryta (an oxide of barium, resembling lime) combined with oxygen at a low temperature, forming a higher oxide (barium dioxide), and that the reverse change took place on raising the temperature. Even this was not a commercial success until improved by Brin. His method is (1) to deprive the air of carbon dioxide by passing it over slaked lime, for otherwise this gas would combine with the baryta and render it useless for the purpose; (2) to heat the baryta to a moderate temperature and pump in air under increased pressure. The oxygen combines with the baryta and the nitrogen remains in the hot iron pipes in which the operation is carried out. The nitrogen is allowed to blow off, and (3) the pumps are reversed and made to diminish the pressure below the normal. Oxygen comes off and is collected in a holder. Baryta remains and the process is repeated. The changes may be represented thus:—



This process has just become obsolete since it has been found better to use liquefied air. When this liquid is allowed to boil by exposing it to normal pressure the nitrogen evaporates first almost entirely and the oxygen last. The latter is collected and compressed into steel cylinders for use in hospitals, laboratories, &c. It contains about 97% of oxygen and 3% of nitrogen.



Baryta

Barium dioxide.

The fact that nitrogen comes off first and then oxygen, indicates that the air is a mixture, not a compound.

Exp. 5. To prepare nitrogen from air and to examine its properties.

Required:—As in Fig. 35; copper-foil or turnings in hard tube, 3 jars.

DIRECTIONS. Pack a piece of hard-glass tube, 25 cm. long, with clean* copper turnings, or better with copper-foil rolled up like a spill. Connect it up as shown in Fig. 35.

Heat the copper gently at first, moving the flame backwards and forwards along the tube, and then more strongly.

Precaution:—*Avoid burning the corks.*

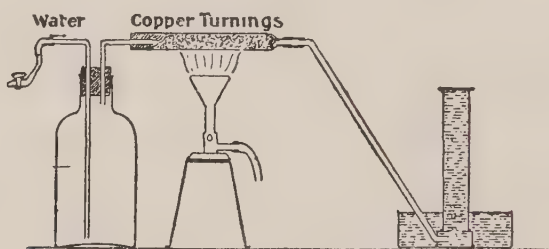


FIG. 35.

Turn on the water-tap so as to drive the air from the bottle *slowly* over the hot copper. Fill three jars.

Put a lighted taper into Jar 1; **note** what happens.

Leave the jar uncovered for three minutes and test again.

Note whether the taper now burns or not.

Add a little clear lime-water to Jar 2 and shake.

Note whether the lime-water is turned milky or not.

Use Jar 3 to find out whether sulphur will burn in nitrogen.

LABORATORY RECORD. Diagram, full observations and *list of the observed properties of nitrogen.*

Questions:—(i) Why was the copper well heated *before* passing air over it?

(ii) Why was the air passed over *slowly*?

(iii) What is the black substance seen on the copper after cooling?

(iv) Do you expect that the contents of the tube have altered in weight?

(v) How can nitrogen be distinguished from carbon dioxide?

* The turnings must have been cleansed from oil by means of caustic soda and alcohol.

Exp. 6. To find how many c.c. of oxygen there are in 100 c.c. of air.

Required:—Tube (40 cm. long), wire, yellow phosphorus, and jar, as in Fig. 36 a; burette, rubber band, taper, test-tube.

DIRECTIONS. *A.* Find the volume of the long tube by means of a burette.

Read the temperature and pressure of the air in the room. Transfer (with tongs) a small piece of yellow phosphorus to a small test-tube half full of water, and warm it very gently until the phosphorus melts (M.P. 44° C.).

Bend one end of a piece of wire into a loop, dip it in the melted phosphorus and cause the latter to solidify by holding the test-tube under the tap.

Precautions:—*Do not touch the phosphorus with your fingers and do not keep it long in the open air.*

Place the phosphorus in the tube and arrange as in Fig. 36.

Observe (*a*) the phosphorus, (*b*) the level of the water in the tube, at intervals. Leave it for three or four days.

B. Fill the jar to the brim with water, and, having fixed a clamp to the tube to hold it by, slip on a rubber band. Raise the tube until the levels of the water inside and outside are the same, and mark the level by means of the band. Withdraw the wire and phosphorus from the tube without removing the latter from the water.

Read the barometer and take the temperature of the air. Close the open end of the tube with the finger, remove it from the jar, and place it right side up without allowing any water to escape.

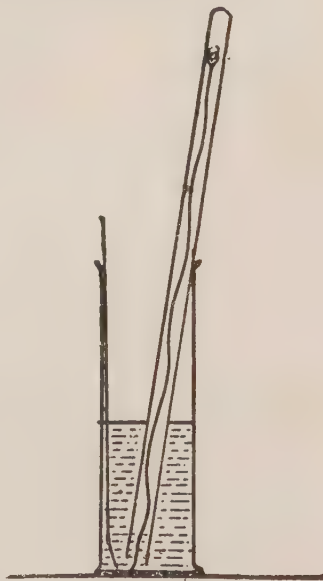


FIG. 36 a.

Remove the finger and at once put in a lighted taper.

Pour out the water and find the volume up to the band by means of a burette. This gives the volume of residual gas, at the temperature and pressure noted.

LABORATORY RECORD. Diagram; enter measurements thus:—

Volume.	Temperature.	Pressure.	Volume at <i>T</i> and <i>P</i> .
Of air taken = — c.c.	$T^{\circ}\text{C.}$	$P\text{ m.m.}$	
Of residue left = — c.c.	$—^{\circ}\text{C.}$	— m.m.	*

Calculate as follows:—

$$\begin{array}{lcl} \text{Volume of air taken} & = & x \text{ c.c.} \\ \text{(corrected) } \quad \quad \quad \text{,, } \quad \text{,, residue left} & = & y \text{ c.c.} \end{array}$$

$$\therefore \text{volume of oxygen} = x - y \text{ c.c.}$$

In x c.c. of air $x - y$ c.c. are oxygen.

$$\therefore \text{In } 1 \text{ ,, ,, ,, } \frac{x-y}{x} \text{ ,, ,, ,,}$$

$$\therefore \text{In } 100 \text{ ,, ,, ,, } \frac{x-y}{x} \times 100 \text{ c.c. are oxygen.}$$

Questions:—(i) Out of five volumes of air, how many are (approx.) oxygen, and how many nitrogen? State the percentage of each gas present in air.

(ii) Did the phosphorus burn? Was there a flame?

(iii) Of what did the fumes consist, and what became of them?

(iv) Why is it necessary to observe the temperature and pressure of the atmosphere (*a*) when the experiment is started, (*b*) on reading the final volume, in order to obtain accurate results?

PROBLEM (VIII. 6). Find the percentage volume of oxygen in air obtained from your breath. Compare it with that of ordinary air.

* If the thermometer and barometer readings in *B* were different from those in *A*, this volume must be corrected by finding what it would become at the first temperature and pressure. (See p. 68.)

To find the gravimetric composition of air, as regards oxygen and nitrogen. Fig. 36 b shows the apparatus, consisting of a glass globe (B) from which the air has been extracted by an air-pump. The globe is connected with a hard-glass tube (A), packed with copper turnings and heated by a furnace. The hard tube is attached to a series of tubes containing substances to remove carbon dioxide, water vapour, and any accidental impurities.

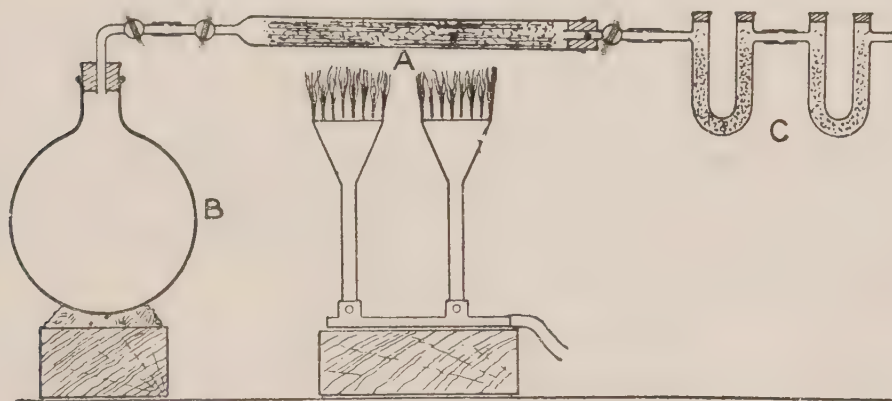


FIG. 36 b.

The water vapour is always taken out last, because some of the other tubes contain water; oxide of phosphorus and sulphuric acid are used for this purpose, and caustic potash is used to absorb carbon dioxide.

The air in both A and B is pumped out, and each vessel is weighed separately. They are then fixed in position and the copper is well heated. After this the taps are all partly opened so that air enters slowly through the purifying tubes c. The oxygen combines with the copper, while the bulk of the nitrogen passes on to B. A little nitrogen, however, remains in A. When B is filled with nitrogen at the atmospheric pressure no more air enters c and all the taps are closed. After cooling, further weighings are made as shown below:—

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To absorb CO_2	Caustic Potash	To absorb H_2O	$\left. \begin{array}{l} \text{Sul. H}_2\text{SO}_4 \\ \text{Calcium Chloride} \\ \text{P}_2\text{O}_5 \end{array} \right\}$
	Caustic Soda		

Weighings.

Globe B, with nitrogen, after exp.	=	w g.
„ „ exhausted, before exp.	=	v g.
Wt. of nitrogen collected in B	=	$w - v$ g.
Tube A, with nitrogen, after exp.	=	x g.
„ „ exhausted „ „	=	y g.
Wt. of nitrogen collected in A	=	$x - y$ g.
<i>Total weight of nitrogen</i> = $(w - v) + (x - y)$ g.		
Tube A, exhausted, after exp.	=	y g.
„ „ „ before exp.	=	z g.
<i>Total weight of oxygen</i>	=	$y - z$ g.

The total weight of purified air used is found by adding the total weight of nitrogen to that of oxygen.

By this method Dumas and Boussingault found in 1841 that the gravimetric composition of air is—

Oxygen	23	parts	by	weight.
Nitrogen	77	„	„	„
Air	100	„	„	„

Other gases contained in air. Besides nitrogen and oxygen, air always contains a small quantity of carbon dioxide (about 0.035 %), varying amounts of water vapour, and minute quantities of other gases, e.g. ozone, ammonia, &c.

About 1894 Lord Rayleigh noted that a litre of atmospheric nitrogen weighed 1.2572 g., whereas a litre of nitrogen obtained in other ways only weighed 1.2505 g. As a result of this observation it was suspected that atmospheric nitrogen, i.e. air from which water vapour, carbon dioxide, oxygen, and accidental impurities had been removed, contained some gas like nitrogen but of greater density. Professor Ramsay joined in the research, and by 1898 five new gases had been detected. They had been previously overlooked because they are even more inactive than nitrogen, i.e. they did not combine with copper or other substances and were weighed along with the nitrogen in the experiment described on p. 113.

Their names are argon (lazy), neon (the new one), krypton (the hidden one), xenon (the stranger), and also helium (the sun). The latter was found by Professor Ramsay, and had been previously known to exist in the sun.

Out of 77 parts by weight of 'atmospheric nitrogen' about 76 are pure nitrogen, the five new gases making up 1 part only. The percentage of xenon in air is only 0.0000026, or 1 part in 38,461,538 parts of air.

After removing the oxygen by passing air over hot copper, a large portion of the nitrogen was removed by passing the residual air over hot magnesium. Magnesium combines with nitrogen but not with the new gases. [When magnesium burns in air and the oxygen has been reduced in quantity by the formation of magnesium oxide, a yellow solid—magnesium nitride—begins to form if the temperature is sufficiently high.]

Exp. 7. To find whether ordinary water contains dissolved air.

Required:—500 c.c. flask or tin can, &c., as in Fig. 37.

DIRECTIONS. Take the flask or tin can, and fit it up as in Fig. 37. The end of the delivery-tube in the flask must not protrude below the cork. Fill it to the brim with tap-water. Fill the delivery-tube also by sucking up water into it. Close the end dipping into the water, and then the other end with your finger. Press the cork into the mouth of the can and see that the apparatus is quite full of water to the end of the delivery-tube.

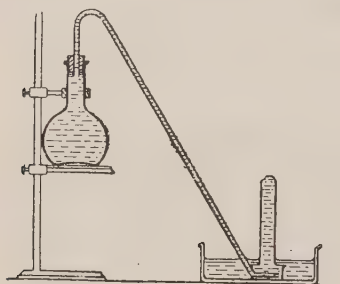


FIG. 37.

Heat the flask till the water boils, collecting any gas that may escape from the delivery-tube in a test-tube standing in the trough. Devise a means of showing whether it is air or not; if approved, try it.

LABORATORY RECORD. Diagram; observations, not omitting difficulties encountered and overcome.

Questions:—(i) How is it that the gas enters the test-tube?

Why does it not remain at the top of the boiled water, or in the tube?

(ii) By what tests did you find whether the gas was air or not?

(iii) Does the solubility of a gas in a liquid increase or decrease as the temperature rises?

(iv) Why did not the extracted gas re-dissolve in the water in the trough?

PROBLEMS (VIII. 7). 1. Devise a way for finding out the volume of air dissolved by a litre of tap-water at the air temperature; if approved, carry it out.

2. Determine the percentage volume of oxygen in the gas obtained from tap-water.

QUESTIONS ON CHAPTER VIII.

1. Give a list of substances from which oxygen can be obtained by the action of heat. Describe *fully* the common laboratory method of obtaining the gas.

2. Explain clearly how you could show that when a mixture of potassium chlorate and manganese dioxide is heated, the oxygen comes from the former and not from the latter.

3. Calculate the percentage weight of oxygen obtainable from mercury oxide, nitre, and potassium chlorate, using the following data :—

5.4 g. of mercury oxide	yielded 0.4 g. of oxygen.
5.05 „ nitre	„ 0.8 „ „
12.25 „ potassium chlorate	„ 4.8 „ „

4. Describe experiments you would do to prove that the substance left after heating potassium chlorate is different from the unheated substance.

5. Given a black powder, how would you discover whether it was carbon or manganese dioxide, or a mixture of both?

6. How may oxygen be freed from traces of carbon dioxide and water vapour?

7. By what special characteristics would you distinguish between oxygen, carbon dioxide, sulphur dioxide, and nitrogen?

8. How is oxygen obtained from the air on a manufacturing scale?

9. In Exp. 4 the following results were obtained :—

Weight of tube + potassium chlorate before heating = 35 grams.

Weight of tube „ „ after heating = 34.2 grams.

Volume of water expelled from flask = 509 c.c.

Temperature of the air = 15° C.

Calculate the density of oxygen (a) at 0° C., (b) at 15° C.

10. Explain why it is easier to obtain nitrogen than oxygen from air. How is the former done? Why is copper used, in preference to phosphorus and sulphur, for getting rid of the oxygen?

11. State the properties of (a) nitrogen, (b) oxygen, as far as you have observed them.

12. The metal calcium when hot absorbs nitrogen; describe how you would carry out an experiment to extract the argon from atmospheric nitrogen. (Calcium does not combine with argon.)

13. Describe briefly how the volumetric composition of air (as regards oxygen and nitrogen) can be determined.

14. Explain fully how the gravimetric composition of air can be ascertained.

15. Describe how dissolved gases can be extracted from tap-water.

CHAPTER IX

FURTHER STUDY OF COMBUSTION RESPIRATION. RUSTING

Summary of previous experiments on burning. So far, quantitative* experiments on burning have been confined to the comparatively simple cases of phosphorus and certain metals, all of which form a solid ash heavier than the unburnt substance. There now remain to be considered substances such as sulphur, carbon, candles, oil, coal-gas, &c., which burn without leaving any visible residue. It will be the main object of the experiments in this chapter to find whether Lavoisier's theory of combustion holds good for them or not.

Record your present knowledge and opinions by answering the following questions in your Fair Notebook. (Copy in the questions also.)

Preliminary Questions on the burning of a candle.

1. Explain what happens to the wax of a candle from the time the wick is lighted until the candle burns out.
2. Under what circumstances does a candle smoke?
3. What is the smoke of a candle? Where does it come from?
4. Does a burning candle use up the air? Give evidence.
5. Would you expect the nitrogen of the air to play any part in the burning?
6. How is it that a candle is 'put out' (*a*) by an extinguisher, (*b*) by blowing it violently?

* The object of *quantitative* experiments is to discover the weights or volumes of the substances which take part in a chemical change. *Qualitative* experiments only aim at discovering the composition of the substances produced—not their quantity.

Exp. 1. To find what is produced when a candle burns in air.

Required:—Small candle, gas-jar, cover-plate, 12 in. of wire.

DIRECTIONS. *A*. Light the candle and hold a small piece of glass tube in the flame. **Note** the deposit on the tube. (This gives a clue to something contained in the candle.)

B. Fasten the candle to a wire; light it and lower it into a jar; cover the mouth of the jar with a glass plate.

Note the appearance of the jar and of the flame.

Raise the candle, relight and lower it again.

Note whether the candle continues to burn. (If it does, repeat the experiment.)

C. Take out the candle, quickly cover the jar again and test the contents for any gas, likely to be present, which would extinguish a lighted taper.

LABORATORY RECORD. Diagram and observations. Description of tests in *C*.

Questions:—(i) Is air altered when a candle burns in it?

(ii) Name all the gases you know which extinguish a lighted taper, and state tests for each.

(iii) Describe the two products of burning you have found (neglecting the smoke), and name them if you can.

(iv) What would you do in order to obtain a proof as to the nature of the products mentioned above?

PROBLEMS (IX. 1). 1. Collect more of the black deposit, and do an experiment with it to confirm the result of *A*.

2. Suggest an experiment to show plainly that air is used up when a candle burns in it. Carry it out, if approved.

3. Devise a means of obtaining a larger quantity of the 'mist' which appeared on the sides of the jar.

Exp. 2. To examine a larger quantity of the mist.

*Required:—As in Fig. 38, aspirator or water-pump. Thermometer, 5 c.c. pipette, wide test-tube, balance, night-light.**

DIRECTIONS. *A.* Set up the apparatus shown in Fig. 38. It consists of a lamp-glass (G) with a cork at the top

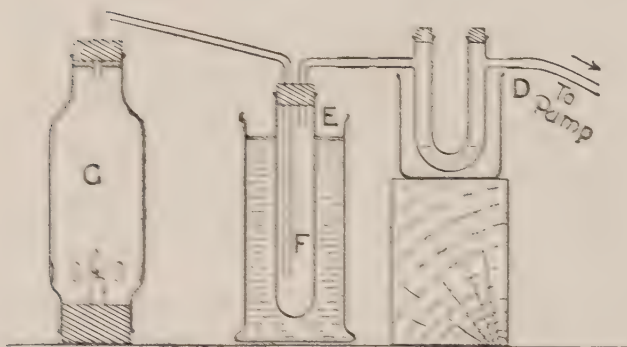


FIG. 38.

through which a glass tube leads into a test-tube (F) standing in a beaker (E) containing water. This connects with a U-tube containing lime-water. The exit-tube D is connected with an aspirator or water-pump*

so that a current of air is drawn through G.

See that all the corks fit tightly and start the pump *slowly*. Light the night-light* and place it in position. Collect 2 c.c. of the liquid. [Keep apparatus for Exp. 3.]

B. Identify† the liquid in F by finding (a) its density, (b) boiling-point (p. 34), and by any other likely test.

LABORATORY RECORD. Diagrams and observations.

Questions:—(i) Name the products obtained.

(ii) Is (a) the gas, (b) the liquid, an oxide or not?

(iii) Does Exp. 2 give any clue to the composition of wax?

(iv) Do you expect the total weight of the liquid and gas to be equal to, greater, or less than the loss in weight of the candle? Why?

* See Appendix.

† Enough liquid for this purpose can be obtained by adding the contents from several U-tubes together. The determinations can be made by one or two members of the class, but the results should be noted by all.

Exp. 3. To compare the total weight of the products with the loss in weight of the candle.

Required:—As Exp. 2 (A); balance, soda-lime, calcium chloride, asbestos.

DIRECTIONS. Modify the apparatus of Exp. 2 as follows:—Omit the tube F; dry the U-tube and pack half of each limb with *soda-lime*—a mixture of lime and caustic soda, capable of absorbing water and carbon dioxide.

Put large pieces in first till about half full, then smaller ones; shake the tube to make the latter fill the spaces between the former, but avoid packing too tightly.

Fill up each limb with calcium chloride and put a piece of asbestos at the top of each. Find whether you can blow through the tube. (If not, re-pack it more loosely.) Weigh the U-tube and the candle (on the cork) separately. **Record** the weights of both.

Fix the parts together and connect with the pump as in Exp. 2. Light the candle and let it burn for 5 minutes. Then disconnect the pump and allow the apparatus to cool. Reweigh the candle and U-tube.

LABORATORY RECORD. Diagram of apparatus actually used; record observations, including an account of any difficulties.

Wt. of candle <i>before</i> burning = — g.	Weight of U-tube <i>after</i> . = — g.
“ “ “ <i>after</i> “ = — g.	“ “ “ <i>before</i> . = — g.
<i>Loss in weight of candle</i> = — g.	<i>Weight of products</i> . = — g.

Questions:—(i) Is the weight of the products equal to, greater, or less, than the loss in weight of the candle?

(ii) Does your result confirm or contradict your previous opinion? Is the result in harmony with the theory of combustion (p. 129) or not?

(iii) What is the object of the asbestos in the U-tube?

Hypothesis of the composition of wax and water.

The existence of carbon, as soot, in a candle-flame, and the formation of carbon dioxide in the act of burning, show that candle-wax contains carbon. The fact that water is also produced may be explained in two possible ways. The wax contains either (*A*) *carbon and water*, or (*B*) *carbon and some unknown substance X*, which, in the act of burning, unites with oxygen to form water. Both are consistent with the result of Exp. 3.

If *A* is true, then, when the wax burns, only carbon unites with oxygen, while the water is liberated as vapour; if *B* is true, both carbon and *X* combine with oxygen, and water must be an oxide of *X*.

Some experiment must be devised to settle the question. This is especially important, because the answer may give information on the nature of water, a substance that it is desirable to know as much about as possible.

Now, *if A is true*, on burning charcoal (carbon) and a candle, separately, in equal volumes of air, equal volumes of carbon dioxide should be obtained. That is, the carbon of the candle alone will burn, while the water given off will occupy the same space after the burning as it did in the candle before. On the other hand, *if B is true*, the unknown *X* will also unite with oxygen, forming *liquid* water which will occupy much less space than the oxygen gas used to produce it.

If the experiment is done in two equal tubes standing over mercury, then, *if A is true*, in each tube *all* the oxygen will be used to form carbon dioxide which is insoluble in mercury. The level of the mercury inside each tube will be the same. But, *if B is true*, part of the oxygen, in the jar containing the candle, will unite with *X*, forming *liquid* water; hence, the mercury should rise from the trough into this tube to a higher level than in the other.

***Exp. 4.** To compare the effects of burning charcoal and a candle in equal volumes of air.

Required.—As in Fig. 39, A and B; battery, freshly-heated charcoal.

Set up the apparatus shown in A and B, Fig. 39.

In A is a candle having a thin piece of platinum wire placed near the wick. The ends of this wire pass into separate glass tubes containing mercury. By inserting wires from an electric battery at the top of these tubes the candle can be lighted.

In B is a piece of *freshly heated* charcoal surrounded by a platinum wire which can be heated to redness by an electric current as in A.

See that the stoppers are air-tight and that the level of the mercury is the same in each of the lower tubes.

Connect up to the battery and let both the candle and charcoal burn as long as they will. Cool and **note** the levels of the mercury in the lower tubes.

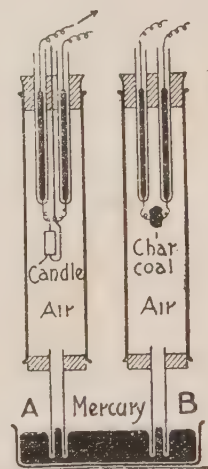


FIG. 39.

Questions :—(i) Which hypothesis explains the result?

(ii) What conclusion do you draw about the composition (a) of wax, (b) of water?

* Demonstration.

Exp. 5. To find what is formed when certain common substances* are burned.

Required:—For A and B, as in Exp. 2; with a U-tube for lime-water, small crucible and absolute alcohol. For C and D, a hard-glass tube, open at both ends, instead of the lamp-glass.

DIRECTIONS. *A. Pure alcohol.* Test the alcohol with white copper sulphate to be sure it is unmixed with water (see p. 50). Support a small crucible (or spirit-lamp made from a flask, singly-bored cork, tube and wick) so as to take the place of the candle in Fig. 38; otherwise the apparatus is the same. Start the air-current and light the spirit.

Note what happens in the tubes, and make any further tests which may be necessary in order to identify the products.

B. Coal-gas. Place a small Bunsen flame under the lamp-glass, and proceed as in *A*.

C. Wood. Instead of the lamp-glass use a hard-glass tube (15 cm. \times 1.5 cm.) drawn out narrower at one end.

Push a piece of *dried* asbestos-wool to the narrow end, and put a small chip of wood near the wide end; attach the narrow end to the tubes and start a rapid current of air through the apparatus.

First heat the tube *between* the wood and the asbestos strongly, and then begin to heat the wood. Heat any part of the tube where any product of burning collects, so as to drive it into the test-tube.

Note (a) what appears in the tubes, (b) whether there is any solid residue in the combustion tube.

Make any further tests required for the identification of the products.

D. Coal. Proceed as in *C*, using a *little* coal-dust.

* These may be distributed among different members of the class. The results, in each case, should be noted by all.

LABORATORY RECORD. Diagrams, observations in *A*, *B*, *C*, *D*.

Questions:—(i) State the names of the products of burning alcohol, coal-gas, coal, and wood. Which leave a solid residue?

(ii) Do you think the solid residue weighs more, or less, than the original substance? Give reasons.

(iii) Do you think that the material of wood consists of one substance or more than one? Answer the question for coal, coal-gas, and alcohol, giving reasons.

PROBLEMS (IX. 5). 1. Devise experiments to find whether the liquid obtained by burning coal-gas is (*a*) a real product of combustion, or merely results from (*b*) the condensation of water vapour contained in the original coal-gas.

2. If water vapour is found mixed with coal-gas, determine whether all the liquid obtained in Exp. 5, *B*, is due to this or only part of it.

Exp. 6. The effect of heating coal in absence of air.

Required:—As in Fig. 40; wire gauze, lime-water, white copper sulphate.

DIRECTIONS. Set up the apparatus shown in Fig. 40, and see that the connexions are air-tight. Wrap wire gauze round A and fill two-thirds of it with powdered coal, and place the flask B in a vessel of cold water, so that any liquid products may be collected. c contains lime-water.

Begin to heat A gently, passing the flame from end to end.

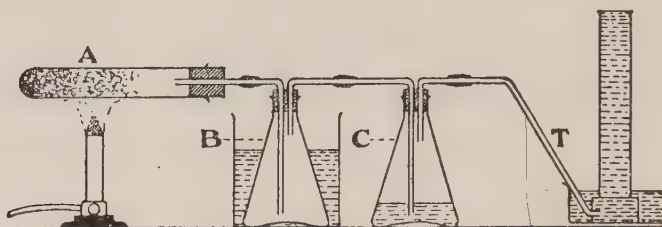


FIG. 40.

Allow time for the displacement of air, then invert a jar, full of water, over the end of T. Continue heating until bubbles of gas *cease* to escape from T.

Note whether (a) the lime-water is affected; (b) a liquid has collected in B; if so, smell it and test for water.

Remove the gas-jar, using a cover-glass. **Note** the smell of the gas, and find whether it burns.

LABORATORY RECORD. Diagram and observations.

Questions:—(i) Did carbon dioxide pass into c?

(ii) Are other liquids produced in addition to water?

(iii) What name is commonly given to the inflammable gas produced?

(iv) What is the residue left in the tube?

PROBLEM (IX. 6). Repeat Exp. 6, using wood.

Dry distillation. The above process of heating solids in absence of air and collection of the products is known as *dry* or *destructive distillation*.

Exp. 7. To find whether the ash from wood or coal weighs more or less than the original wood or coal.

Required:—Crucible, chips of wood, coal, balance.

DIRECTIONS. *A.* Put a few chips of wood in a small crucible and weigh.

Fix it on a pipe-clay triangle resting on the ring of a retort-stand. Heat with a low flame until the wood seems completely burnt. Cover with a lid and, when cold, reweigh without the lid.

B. Repeat *A*, using a *small* quantity of powdered coal.

LABORATORY RECORD. Diagram, weighings, and observations.

Questions:—(i) Is the ash lighter or heavier than the wood or coal used? Does the result agree, or disagree, with your previous opinion?

(ii) Suppose the wax used to make a candle had been mixed with some fine white sand, would you expect a solid residue to be left after burning such a candle or not?

(iii) If so, would you expect this residue to weigh the same as the sand or not?

(iv) Knowing that a tree must get all its material for forming wood from (*a*) water which has passed through soil, and (*b*) air, do you think it possible that the wood does contain some incombustible material?

(v) Knowing that coal is fossilized wood, are the same arguments as likely to apply to coal-ash as to wood-ash?

(vi) Do you think it more likely that the ash from wood (*a*) is the oxide of some combustible solid contained in the wood, or (*b*) that it is incombustible matter mixed with the combustible material of the wood? Give reasons for your answer.

PROBLEM (IX. 7). Find the percentage weight of ash from wood or paper.

Hypothesis of the composition of wood, coal, and alcohol.

The combustion of wood and coal in air has proved to be more complex than that of a candle, since *three* products are formed—water, carbon dioxide, and a *solid ash*.

When heated out of contact with air there is no burning, but each breaks up into a variety of substances. Thus, from coal are obtained:—*coal-gas, water, coal-tar, and coke*; and from wood:—*an inflammable gas, water, wood-tar, and charcoal*.

This process, of heating bodies in absence of air (dry distillation), differs entirely from burning, since there is no combination of the heated body with oxygen. Most of the products formed are capable of burning in air, e. g. the gas, the tar, and the coke. The first two yield water and oxide of carbon, and coke yields oxide of carbon and leaves an incombustible ash lighter than the original coke.

Since water is formed by dry distillation, and since it is probable that water is an oxide (p. 123), it follows that wood and coal contain a certain amount of oxygen. The conclusion may therefore be drawn that coal and wood contain—

- | | |
|--------------------------------------|-----------------------------|
| A. Carbon ; | C. A little oxygen ; |
| B. The substance <i>X</i> (p. 122) ; | D. The ash (or part of it). |

It may further be supposed that, on dry distillation, the gas and combustible tarry liquid are derived from *A* and *B* and perhaps *C*; the water from *B* and *C*; the coke or charcoal from *A* and *D*.

By similar reasoning, the conclusion follows that alcohol contains carbon, the unknown *X*, and perhaps some oxygen.

Extension of our theory of combustion. Although the principle underlying the statement of the theory on p. 93 is true for all the cases of combustion we have studied, the theory itself requires to be stated in more accurate terms, so as to explain the quantitative, as well as the qualitative, facts of combustion.

It has been seen that oxides may be solid, like magnesium oxide, or gaseous, like carbon dioxide, and possibly liquid, if water is an oxide. Therefore instead of the word 'ash', which implies a solid body, the word 'oxides' must be substituted, so as to include gases and liquids, and to indicate that more than one product may be formed. Hence the **theory of burning** may now be stated thus:—*When a material burns in air, it wholly or partly unites with the oxygen, producing one or more oxides which, together, weigh more than the combustible part of the original material, by the weight of the oxygen added.*

If the material consists of an incombustible as well as a combustible part, the former will be left over after the burning. This part will naturally be lighter than the whole original material.

The preceding experiments have dealt only with the action of combustibles *in air*. It is well known, however, that certain substances seem to be able to burn without air. For instance, a fuse, consisting of a train of gunpowder in an air-tight casing, will burn under water, where no air can get to it. As this appears contradictory to the theory expressed above, the object of the next experiments will be to clear up this point.

Exp. 8. To find how some substances can burn without air.

Required:—Hard-glass test-tube, singly-bored cork to fit, quill tubing, nitre, lime-water, wooden splinters.

DIRECTIONS. *A.* Fit a right-angled tube to the cork and place it by you on the bench. Put a little nitre in the hard-glass test-tube and heat it strongly. **Note** whether (*a*) the nitre melts, (*b*) any gas escapes. Find whether a glowing splinter is relighted when placed at the mouth of the tube.

B. Quickly drop into the hot nitre a fragment of charcoal, press the cork carrying the right-angled tube into the mouth of the test-tube and heat the nitre strongly.

Let the end of the right-angled tube dip into an empty test-tube.

When the action is over pour a little lime-water into the open test-tube; close with your thumb and shake.

Note what happens.

LABORATORY RECORD. Diagram and observations in *A* and *B*.

Questions:—(i) What gas is produced by heating nitre?

(ii) What gas is produced by heating charcoal with nitre?

(iii) Give reasons for supposing that the nitre actually loses what the charcoal takes.

Exp. 9. The action of melted nitre on sulphur and charcoal.

Required:—Sulphur and powdered charcoal, nitre, pipe-clay triangle, crucible (oo), tile.

DIRECTIONS. *A.* Arrange the crucible as in Fig. 25, p. 79. Fill one-third of it with nitre and melt it with a small flame.

Add a small fragment of sulphur and **note** the result.

B. Put some more nitre into the crucible and repeat *A*, using a *small* quantity of a mixture of powdered charcoal and sulphur. **Note** the result.

Precaution:—*Keep your face away from the crucible.*

LABORATORY RECORD. Observations in *A* and *B*.

Questions:—(i) Why do sulphur and charcoal burn more rapidly when mixed with nitre than when heated alone in air?

(ii) Is melted nitre a supporter of combustion?

(iii) Would you expect combustion to occur if a mixture of charcoal, nitre, and sulphur were heated in absence of air?

(iv) Are the facts ascertained about combustion in absence of air contradictory to the main idea of the theory of combustion stated on p. 129?

PROBLEM (IX. 9). Devise a method for separating gunpowder into nitre, sulphur, and charcoal. Identify each substance, when separated, by suitable tests. Submit your plan for approval before starting. (See pp. 38, 39.)

Combustion in the absence of air. The facts observed in Exps. 8 and 9 show that combustibles, such as charcoal and sulphur, will burn without air if they are mixed with a substance, like nitre, which yields oxygen on heating. Once the mixture is sufficiently heated, very rapid combustion occurs, and large volumes of hot gases are generated. There is nothing contradictory to the main idea of the theory stated on p. 129; it is only necessary to omit the words 'in air' to make it applicable.

Materials, like gunpowder, containing both combustibles and plenty of oxygen, form a class of bodies known as explosives. When they are burnt in a confined space the rapidly generated gases exert an enormous pressure. This pressure is employed for propelling shells from guns, in blasting rocks, and many other purposes.

Combustibles and supporters of combustion. It has been seen that oxygen plays quite as important a part in combustion as the combustible itself. It will be interesting to observe what happens when a flame is applied to a jet of air passing into a vessel full of coal-gas.

Exp. 10. To find whether air will burn in coal-gas.

Required:—Apparatus shown in Fig. 41; disk of a deflagrating spoon.

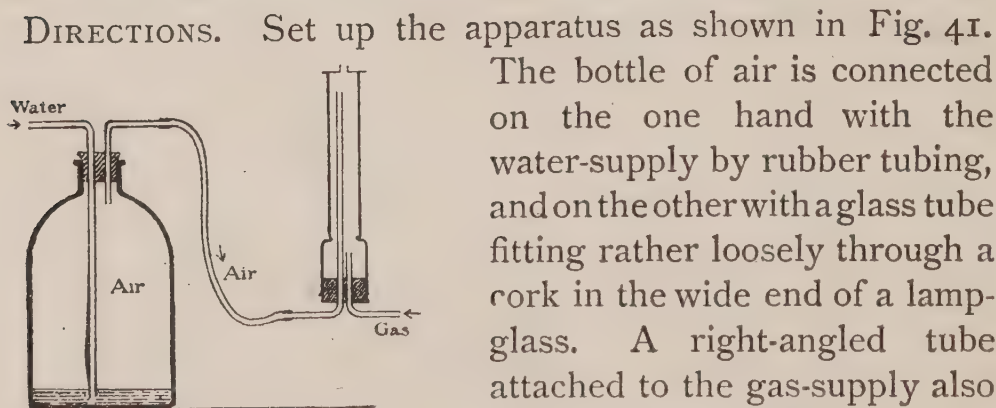


FIG. 41.

The bottle of air is connected on the one hand with the water-supply by rubber tubing, and on the other with a glass tube fitting rather loosely through a cork in the wide end of a lamp-glass. A right-angled tube attached to the gas-supply also passes through this cork.

The lamp-glass is supported by a clamp on a retort-stand, and the brass disk of a deflagrating spoon (with its cork

removed) is placed on top. The long tube is pushed through the cork until the upper end is near the disk.

Now turn on the gas and ignite it at the hole in the disk, so that it burns with a small flame, and by allowing water to enter the bottle, cause a slow stream of air to pass into the lamp-glass.

Note whether any flame appears at the top of the long glass tube. If so, draw the tube down so that the flame is in the middle of the lamp-glass. If no flame appears, put the tube up again so as nearly to touch the disk. Then lower it. If there is a flame, **note** its colour.

Precaution :—*Take care that the water-tap is turned off before the bottle is full of water.*

LABORATORY RECORD. Careful diagram; full notes on the experiment, not omitting difficulties met with.

Questions :—(i) Will air burn in coal-gas? If so, which is the combustible substance, and which the supporter of combustion?

(ii) In what respects did the flame which burned on the end of the long glass tube resemble that of a Bunsen burner?

PROBLEMS (IX. 10). 1. Find whether a lighted taper continues to burn when it is pushed up into an inverted jar of coal-gas.

2. Partly fill a gas-jar with coal-gas by displacement of water. Let the rest of the water run out so as to fill the remaining space with air. Cover the mouth of the jar with a glass plate, and find the effect of applying a lighted taper to the contents. Repeat, using different proportions of air and gas, noting the difference in the results. Try to explain them.

The dual nature of combustion. Exp. 10 has shown that it is quite as correct to say that 'air burns in coal-gas' as that 'coal-gas burns in air'. The theory (p. 129) supports this view, since it recognizes that the parts played by the 'combustible' and 'supporter of combustion' are *equal* in importance. If either is absent there can be no burning. In general, it is found that if a jet of any gas *A* will burn in an atmosphere of any other gas *B*, then a jet of *B* will burn in an atmosphere of *A*. Hence the terms 'combustible' and 'supporter of combustion' are reversible for gases, i. e. they are relative terms.

Flames. From the earliest times flames have been considered mysterious objects. The foregoing experiments show that they are the region of chemical changes which occur at the surface of contact between the combustible and the gaseous supporter of combustion.

A **Flame** may be described as *a region of rapid combustion in which gases, and often solids, are rendered more or less luminous by the heat which is always evolved.*

In Chap. I it was found (a) that the shape of a coal-gas flame depends on the shape and position of the holes through which the gas issues; (b) that the different parts of a flame are not all equally hot; and (c) that when coal-gas is previously mixed with air, as in a Bunsen flame, very little light is emitted. Some further points will now be considered.

Preliminary Questions on Flame.* 1. Which is the hotter—the inner or the outer cone of a Bunsen flame?

2. What substances are formed when coal-gas burns?

3. Why is soot present in the flame of a candle and in a luminous coal-gas flame, but not in the Bunsen flame?

4. Why is the luminous flame larger than the Bunsen flame from the same burner?

5. Under what circumstances does a Bunsen flame strike back, and burn near the air-holes? Why does this happen, and why does it not happen when the air-holes are closed?

6. Under what circumstances can the flame of a Bunsen burner pass through wire gauze? Why does it not do so as a rule?

* To be answered, in the Fair Notebook, from general knowledge.

Exp. II. To examine the structure of flames.

Required:—Quill tubing, washing soda, splinters, tongs, candle.

DIRECTIONS. *A.* Close the air-holes at the base of a Bunsen burner.

Light the gas, and hold a narrow piece of glass tubing (8 cm. long) with tongs, so that the lower end of the tube is in the middle of the flame, just above the burner, and the upper end is outside the flame. (See Fig. 42.)

Bring a light to the upper end of the tube.

Note the result.

Repeat, using the Bunsen flame.

B. Char the end of a wooden splinter and soak it in a solution of washing soda; bring the charred end into the extreme edge of a steady luminous flame. **Note** that the soda colours a part of the flame which was invisible before.

Repeat, using the Bunsen flame.

C. Hold a short glass tube in the luminous flame, and **note** the black deposit of soot. Open the air-holes, keeping the tube still in the flame; **note** what happens to the soot.

D. Examine the structure of a candle-flame and draw a diagram showing the different zones. Compare it with the luminous flame from a Bunsen burner.

LABORATORY RECORD. Diagrams to show the structure of the flames of a Bunsen burner when the air-hole is (*a*) open, (*b*) closed, and of a candle. Observations in *A*, *B*, *C*, and *D*.

Questions:—(i) Give reasons for supposing that the inside of a gas-flame, near the top of the burner, contains unburnt gas.

(ii) How do you account for the presence of a nearly invisible mantle surrounding a luminous gas-flame?

(iii) Why does the soot disappear in *C*?

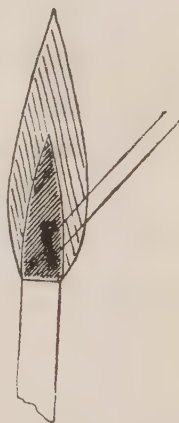


FIG. 42.

Note on the structure of flames. Exp. II, together with those in Chap. I, show that a *luminous coal-gas flame* consists of four parts, as represented in Fig. 43:—

- (a) the blue portion at the base;
- (b) the cold dark region of unburnt gas;
- (c) the hot luminous zone of gas in the act of burning;
- (d) the non-luminous mantle, the hot region of complete combustion.

On gradually admitting air, the size of the flame as a whole diminishes; *a* and *d* increase, while *c* diminishes until it finally disappears. (See Fig. 44.)

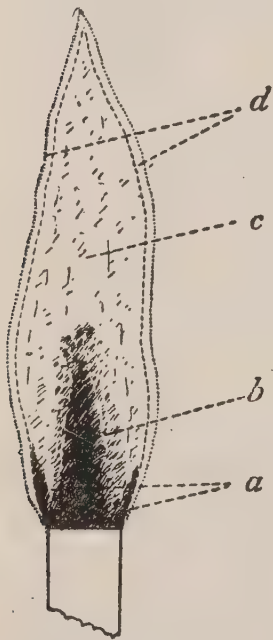


FIG. 43.

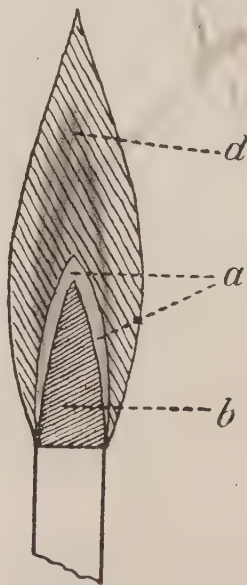


FIG. 44.

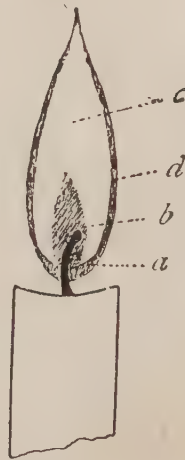


FIG. 45.

So the *Bunsen flame* consists of three zones:—

- (i) cold unburnt gas *b*;
- (ii) a hot blue portion *a* surrounding *b*;
- (iii) the mantle *d* surrounding *a*.

The introduction of air makes the flame hotter, and prevents the deposition of soot; in fact we have seen that there is enough air in a Bunsen flame to burn away soot placed in it.

A *candle-flame* (Fig. 45) is similar to a luminous gas-flame, except that it is narrower near the base, as the gases come from a narrow wick.

Exp. 12. To use the Bunsen flame as a means of distinguishing certain solids.

Required :—Platinum wire fused into a glass holder, lead-pencil, emery-paper, dilute hydrochloric acid, copper oxide, copper wire, blue vitriol, and substances mentioned in E below.

DIRECTIONS. *A.* Make a loop on a piece of *copper* wire, dip this in a few drops of hydrochloric acid, and hold it in the Bunsen flame at a point about two-thirds of its height near the edge.

Note the colours produced.

B. Cut away the wood of a lead-pencil, leaving an inch of black-lead exposed. Dip it into a few drops of *pure* acid in a watch-glass, and then into a little copper oxide. Hold it in the flame and **note** the colours. Moisten again with acid and replace in the flame.

C. Clean the lead-pencil and repeat *B*, using powdered blue vitriol and *fresh* acid.

D. Make a small loop at the end of a piece of platinum* wire and dip it into a little dilute *hydrochloric acid*.

Place it in the flame. **Note** whether any persistent colour appears. [If so, clean the wire with emery-paper and repeat.] When clean, use it to observe the coloration imparted to the flame by potash alum, remoistening with acid when the colour becomes faint.

E. Repeat *D*, using a *clean wire* and *fresh acid* in each case, and observe as much as you can about the effects (whether in colouring the flame, melting, glowing, or colour of residue) of the following white substances :—
(a) *nitre*, (b) *calcium chloride*, (c) *barium chloride*, (d) *strontium carbonate*, (e) *common salt*, (f) *soda*, (g) *lime*, (h) *magnesium oxide*, (i) *zinc oxide*, (j) *aluminium oxide*.

* Platinum wire should not be used for compounds suspected to contain copper, lead, tin, antimony, as they form brittle alloys, and so destroy the wire.

F. Cobalt nitrate tests. Compounds of some metals do not give a well-marked flame coloration, but the solid glows brightly, like an incandescent gas-mantle, e.g. compounds of magnesium, zinc, and aluminium. [Oxides of calcium, strontium, and barium also glow, but they give distinctive colours to the flames.] The first three may be distinguished by heating on a platinum wire (or on charcoal with a blow-pipe flame), then moistening with a drop of cobalt nitrate solution and reheating. Perform this test with oxides of magnesium, zinc, tin, and aluminium, and **note** the colour of the residue. Repeat with Epsom salt, alum, and zinc sulphate.

LABORATORY RECORD. Arrange observations thus :—

Name of substance.	Colour imparted to the flame (if any).	Any other effect noticed, such as glowing, change of colour, swelling of the solid.
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- Questions* :—(i) Seeing that both copper and copper oxide give a similar flame coloration, it is plain that the colour is due to the metal ; what metal does blue vitriol contain ?
- (ii) How can you distinguish between potash alum, soda, and compounds of calcium, barium, and strontium ?
- (iii) How can you distinguish between magnesium oxide, zinc oxide, tin oxide, lime, and aluminium oxide ?
- (iv) Can you draw any conclusion from the similarity of the flame colorations of soda and common salt, and from the appearance of the residue in the cases of magnesia and Epsom salt ? If so, what ?

Air and animal life. It is generally known that men and animals cannot live without a constant supply of fresh air, any more than a candle can burn without it. This common dependence on fresh air points to some similarity between the processes of respiration and burning. The object of the next experiment is to find how far this similarity extends.

Exp. 13. To find whether exhaled air differs in composition from inhaled air.

Required:—As in Fig. 46 ; lime-water.

DIRECTIONS. *A.* Set up apparatus as shown in Fig. 46, but with the flasks empty and dry.

Put the tube *t* in the mouth, and having closed the exit-tube from one flask with the finger, *exhale* air through the other flask. Now close the exit-tube of the flask through which you have just been breathing and *inhale* air through the other. Continue this for several

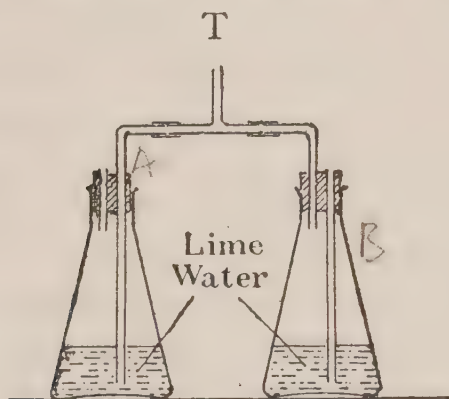


FIG. 46.

minutes. **Note** whether anything has collected in either flask, and if so, find out what it is.

B. Clean out both flasks thoroughly, by washing with water, and put lime-water into each. Place the tube *t* in the mouth as before, and inhale air so as to cause it to bubble through the lime-water in one flask, and then exhale air so as to drive it through the lime-water in the other flask ; continue to do this for a few minutes. **Note** whether the lime-water is changed in either flask.

LABORATORY RECORD. Diagram and observations.

Questions:—(i) What two products do you find in exhaled air ?

(ii) Are they present also in inhaled air ? If so, are they present in the same quantities ?

(iii) Give examples of substances which, when burned, yield the same products as the act of breathing.

Air and plant life. Exp. 13 shows that the two main products of animal respiration are the same as those produced by the combustion of a candle, alcohol, oil, &c. Hence breathing, from a chemical point of view, closely resembles slow combustion. All these processes will increase the quantity of carbon dioxide in the air.

It is well known that plants also require air for their proper growth—do they use it in the same way as animals? Experiments show that if freshly cut green leaves are immersed in water and exposed to sunlight, small bubbles of gas are evolved. On collecting and testing this gas it turns out to be oxygen. If carbon dioxide be bubbled into the water until it is saturated, after a time the leaves give off more oxygen. The green leaves of plants therefore have the power of taking in carbon dioxide from the air in sunlight and of giving out oxygen. The carbon remains in the plant combined with other substances. A plant obtains all its carbon from the air through the *stomata* (little mouths) on the under-side of the leaves. The general effect of vegetation on the air is to take in carbon dioxide and give out oxygen, thus preventing the undue accumulation of carbon dioxide resulting from the respiration of animals, burning, ferments in the soil, volcanic action, &c. Sea-water also dissolves carbon dioxide in large quantities.

The rusting of iron. It is a matter of common knowledge that iron when left in the open air becomes coated with rust. It will be of interest to find out what rust is and whether its formation has anything to do with oxygen, or whether it depends on some other substance in the air.

*Preliminary Questions.** 1. Do you think that rust contains iron, or is merely a deposit of something which contains no iron?

2. How would you propose to find out which, if any, of the gases in the air are concerned in the process of rusting?

3. Mention any other metals which rust.

4. Do you think that the weight of a piece of rusty iron differs from that of the iron before rusting?

5. Does iron rust best in moist, or in dry, air?

6. Does iron rust when it is covered with water?

7. What are the best conditions for rusting?

8. Do you think that rusting is caused (*a*) by the action of the air alone, (*b*) by the action of water alone, (*c*) by the joint action of the two, or (*d*) by some other action?

9. What is the colour of the iron oxide obtained by burning iron in oxygen? Is it the same as that of iron rust?

* To be answered, in the Fair Notebook, from general knowledge.

Exp. 14. To find whether air is used up when iron rusts, whether the presence of water is necessary, and whether the rust differs in weight from the original iron or not.

Required:—Iron filings, 2 flasks, 2 basins, desiccator, balance, corks, beakers.

DIRECTIONS. *A.* Moisten the inside of a flask with water, add a few iron filings and shake them so that they adhere to the flask. Invert it in a beaker of water and leave alone for a week.

B. Sprinkle a few clean iron filings into each of two small evaporating dishes (*X* and *Y*) so as to form a thin layer. Weigh both and **record** figures. Put *X* in a desiccator; moisten the filings in *Y* with a few drops of water. Let both remain for a week.

C. After a week has elapsed, examine the flask in *A*. **Note** any obvious changes. Cork up the flask while its mouth is still under water, and place it upright on the bench. Uncork it and at once insert a lighted taper. **Note** the effect. If there is water in the flask, measure its volume and also the volume of the whole flask.

D. Put the dish *Y* in a steam-oven for half an hour, cool, and reweigh.

Reweight *X* while *Y* is in the oven.

Record both weighings.

LABORATORY RECORD. Full observations and weighings. In *C* calculate the percentage volume of air which has disappeared.

Questions:—(i) Does air disappear when iron rusts in it? If so, what proportion?

(ii) Does iron rust in dry air? Is moisture necessary for rusting or not?

(iii) Is the weight of rust the same, greater, or less than that of the original iron?

(iv) What objection is there to the result of *D* if the drying is not complete? How can you be certain that it is complete?

PROBLEMS (IX. 14). 1. Find whether iron will rust in (*a*) recently boiled distilled water, (*b*) ordinary tap-water. Place filings in two jars and fill up with each kind of water. Invert them in a dish of mercury, leaving the covers on the jars, and allow them to remain for a week.

2. Repeat 1, using aerated water from a syphon. After a week note any change, replace the jar on the bench, and pass a rapid stream of air through the water.

QUESTIONS ON CHAPTER IX.

1. What products are formed when a candle burns in air? Describe how you would collect enough of each for identification, and state what tests you would employ.

2. Give a concise account of a method of proving that the products of the combustion of a candle weigh more than the part of the candle consumed.

3. Explain the grounds for the conclusion that water contains oxygen.

4. How can you show that candle-wax contains (*a*) carbon, (*b*) some other substance?

5. What are the products of the dry distillation of coal? State, as far as you can, the composition of each product, giving clear and concise reasons for your statements.

6. In what way do you account for the fact that the ash of magnesium is heavier than the unburnt metal, whilst the ash of wood is lighter than the unburnt wood?

7. Give instances of mixtures capable of burning without the presence of air. What essential ingredients must they contain?

8. Under what circumstances does gunpowder (*a*) cause an explosion, (*b*) burn quietly?

9. How could you separate and identify each of the constituents of gunpowder?

10. Describe an experiment to show that, in the case of gases, the terms 'combustible' and 'supporter of combustion' are merely relative.

11. Define the term 'flame', and give an account of the structure of a Bunsen flame. What is observed when a Bunsen flame strikes back?

12. Write as complete an account as possible of the changes which go on in a candle from the time it is lighted. Draw a diagram to show the structure of the flame.

13. Give a brief outline of experiments with metallic oxides leading to the establishment of the theory of combustion, and point out how the theory is capable of explaining the burning of coal, and of a fuse under water.

14. Is charcoal pure carbon or not? Give reasons. How would you attempt to find out if soot is pure carbon?

15. When a piece of copper is heated in air it turns black, and when a piece of porcelain is held in a candle-flame it also turns black. How could you show that these two black substances are different?

16. Compare the effects of air on the human body with its effects on a burning candle.

17. Explain carefully how you can prove that a human being exhales water vapour and carbon dioxide. How do you account for the fact that heat is constantly being generated in the bodies of animals?

18. Explain the action of plants on the air. From what sources do (a) plants, (b) animals obtain carbon?

19. Give an account of the conditions favourable to the rusting of iron.

20. The so-called 'tin' in tin cans consists of sheet iron coated with real tin; galvanized iron is iron coated with zinc. Explain the reason for covering the iron, and mention other methods for effecting the same object.

21. How do you account for the fact that phosphorus and iron are not found in the free state in nature, but are almost invariably combined with other substances?

CHAPTER X

THE CLASSIFICATION OF MATERIALS

Preliminary Questions. (*To be answered in the Fair Notebook.*)

1. How would you separate sand and sugar from a mixture of the two? How could the sand be detected before separation?

2. Suppose you were supplied with a mixture of very finely divided iron and powdered sulphur, and were unable to detect the two substances with the naked eye, how could you—

(a) prove the substance to be a mixture;

(b) prove the mixture to contain iron;

(c) separate the iron from the sulphur?

3. Iron rust is known to contain both iron and oxygen. Is it possible to detect the presence of either in the rust?

4. Can mercury oxide be regarded as a *mixture* in the same sense as the sand and sugar in question 1? Give reasons.

5. Draw up in parallel columns the chief properties of mercury oxide, mercury, and oxygen.

6. Compare the effects of heating (a) ice, (b) mercury oxide, with regard to changes in properties and the production of new substances.

7. Classify into two groups the changes which occur during the following actions, according as there is evidence for (i) *the formation of new substances*, (ii) *the absence of new substances, but a change of properties only*. Give brief reasons in each case.

The action of heat on (a) blue vitriol, (b) wood shavings from which air is excluded, (c) zinc oxide, (d) nitre, (e) porcelain; *the burning of* (f) magnesium, (g) a candle, (h) phosphorus; (i) the rusting of iron; (j) the solution of salt by water.

Elements, Compounds, and Mixtures. The materials examined in previous experiments, and in fact all materials, can be divided into two groups, viz. :—

(1) *Simple substances* ; (2) *Complex substances*.

Group 1 is comparatively small, consisting of such materials as iron, lead, mercury, oxygen, and nitrogen, which cannot be resolved, by any known means, into two other simpler substances. These are therefore known as **elements**.

Group 2 is very large ; air, soil, granite, mercury oxide, nitre, &c., are examples. Each of these can be resolved into two or more simpler substances by suitable means. For example, oxygen and nitrogen can be separated from air ; mercury and oxygen from mercury oxide.

By examining the characteristics of the substances in Group 2 more closely, we find that we can subdivide them into two other classes—(a) *those which, like mercury oxide, have properties quite unlike those of their components* ;

(b) *substances, such as air, which retain the properties of their components*.

The substances in class (a) are **compounds** ; those in (b) are called **mixtures**. No one would be led to suspect the presence of mercury or oxygen in the red powder known as mercury oxide, by mere inspection ; but, on the other hand, air has just the properties we should expect it to have, from a knowledge of the properties of its components.

To recapitulate :—all materials may be divided into three classes, *elements, compounds, and mixtures*. Comparatively few elements exist free in nature, the great majority being in a state of combination with others. Nor are these compounds usually found in a pure state, but mixed with others. Such mixtures make up the great bulk of the crust of the earth, and form the raw material for the chemist's work. He extracts pure substances from the mixtures, and decomposes the compounds, so obtained, into elements. Then he builds up other compounds from the elements, and studies their actions on one another.

Elements. About 80 elements have been isolated and are divided into two classes—*metals* and *non-metals*. The following list contains the elements introduced in previous experiments, together with the names of some of the natural substances or minerals from which they are extracted:—

METALS.

Copper, from copper pyrites, a compound of copper, iron, and sulphur found in Cornwall, Spain, America, &c.

Gold, occurs as an element mixed with quartz, in Australia, South Africa, &c.

Iron, from haematite, a natural sort of iron rust, found in Cumberland; it also occurs in iron pyrites, a widely distributed mineral containing iron and sulphur, found largely in Spain.

Lead, from galena, a compound of sulphur and lead, occurring in Wales, Scotland, and the North of England.

Magnesium, occurs in Epsom salts; and in the magnesian limestone of Derbyshire.

Mercury, from cinnabar, a bright red mineral containing sulphur and mercury; it occurs in Spain and Japan.

Silver, from silver glance, its compound with sulphur. It occurs in small quantities, mixed with galena, in England; in large quantities in Mexico.

Tin, from tin stone (oxide of tin), in Cornwall and the Straits Settlements.

Zinc, from zinc blende, a compound of sulphur and zinc, found in Cornwall and the north of England.

NON-METALS.

Carbon, from lamp-black, which is nearly pure carbon; charcoal and coke consist of carbon with a small quantity of ash.

Iodine, from seaweed.

Nitrogen, exists free in the air.

Oxygen, exists free in the air and in combination in a very large number of minerals.

Phosphorus, from bone-ash, formed by heating bones in air.

Sulphur, occurs as an element in volcanic districts, e.g. Sicily, and in many compounds, e.g. iron pyrites, &c.

Some of the differences between the two classes of elements are given below :—

METALS	NON-METALS
have some or all of the following properties :—	have usually :—
(1) <i>Lustre</i> , i.e. they shine.	(1) Little or <i>no lustre</i> .
(2) <i>A high specific gravity</i> .	(2) <i>Small specific gravity</i> .
(3) <i>Malleability</i> , i.e. can be hammered out into thin sheets.	(3) Are <i>brittle</i> (if solid), i.e. they break into pieces when hammered.
(4) <i>Ductility</i> , i.e. can be drawn out into a wire.	(4) Are <i>not ductile</i> .
(5) <i>Great power of conducting heat and electricity</i> .	(5) Are <i>bad conductors</i> .
(6) Are <i>solid</i> , except mercury.	(6) Many are gases, one is liquid (bromine), a few are solid.
(7) The power of combining with oxygen to form <i>basic oxides</i> .	(7) Combine with oxygen to form <i>acidic oxides</i> .
(8) Do not form gaseous or volatile hydrides.	(8) Form gaseous or volatile hydrides.

Complex substances. Reference has already been made to the classification of complex substances as compounds and mixtures. It is most important to have a clear idea of the difference between a *mixture* of two substances and a *compound* of the same substances, since the distinction is not one which would naturally be expected. The following experiments will aim at elucidating this distinction, which involves one of the most striking facts in the science of chemistry.

Hydrides of Non-metals

C_2H_4 .

O_2H_2 ; S_2H_2 .

P_2H_4 ; N_2H_4 .

CH_4 ; Si_2H_6 .

Exp. 1. To examine the properties of iron, sulphur, and a mixture of the two.

Required:—Finely divided iron (ferrum redactum), flowers of sulphur, pestle and mortar, magnet, lens, test-tubes, carbon disulphide, funnel, porcelain basin.

DIRECTIONS. *A.* **Note** the colour and appearance of the iron. Shake with water in a test-tube. **Note** whether it sinks or floats.

Bring a magnet near it. **Note** what happens.

B. Now repeat *A* with sulphur and refer back to your notes on Problem III. 7, p. 39, to find a solvent for sulphur.

C. Put about 5 g. of iron and 4 g. of sulphur in a mortar and pound them together with a pestle, using small quantities at a time till the whole is mixed.

(Reserve half the mixture for Exp. 2.)

Note the colour; action of the magnet; effect of shaking with water; examine it with a lens and find whether any portion is soluble in carbon disulphide.

Precaution:—*No flame must be near the carbon disulphide.*

D. Try to separate pure iron and sulphur from the mixture.

LABORATORY RECORD. Tabulate results thus:—

	Iron.	Sulphur.	The Mixture.
Colour, &c.			
Effect of shaking with water			
Action of magnet . .			
Solubility in carbon disulphide			

Give a description of method and results for *D*.

Questions:—(i) Mention three properties of iron and three of sulphur.

(ii) Are the characteristic properties of iron and sulphur exhibited in the mixture?

[Over.

- (iii) Would the general properties of the mixture be appreciably altered by the addition of a little more iron or sulphur?
- (iv) How can the mixture be separated into the original substances? Mention as many methods as you can.

Exp. 2. To make a compound of iron and sulphur and to compare its properties with those of a mixture of these elements.

Required:—As in Exp. 1.

DIRECTIONS. Half fill a test-tube with the mixture made in Exp. 1.

Lay it over gauze on a tripod and heat it gently, removing the lamp when the mixture gets red-hot. **Note** carefully all that happens.

Hold the tube in the flame (in a draught chamber) and heat strongly, starting at the closed end until the volatile matter has been driven off. When cold, break the tube, place the contents in a mortar.

Pick out any broken glass and grind up the mass.

Note the properties of the substance, which is a compound of iron and sulphur, i.e. its colour; action of magnet; effect of shaking with water; also examine it with a lens.

Find whether any portion is soluble in carbon disulphide.

Try to separate the iron and sulphur by the means adopted in Exp. 1, or in any other way.

N.B.—Keep some of the compound for Problem 1.

LABORATORY RECORD. Tabulate results for both the compound and mixture as in Exp. 1. Full account of the attempt to separate the iron from the sulphur in the compound.

Questions:—(i) In making the compound why was it necessary to drive off all volatile matter before pounding it up? What was the volatile matter?

(ii) Do iron and sulphur retain in the compound (a) all, (b) some of their individual properties? Give details.

(iii) Was it possible to separate the elements in the compound?

(iv) Do you think a given weight of iron will combine with *any* weight of sulphur you choose to take? Give a reason.

PROBLEMS (X. 2). 1. Test your answer to (iv) as follows :—

Put a little of the compound (2 or 3 grams) in a narrow *tube of hard glass* and weigh it. Add a little sulphur, shake it up with the compound, and heat as before till all volatile matter is driven off. Find whether the weight of the tube and compound has altered.

2. Compare the properties of a mixture of *finely divided copper* and sulphur with a compound of the two.

3. Taking a known weight of copper, find what weight of sulphur combines with it. Calculate the percentage composition of the compound.

4. Prepare lead iodide by gently heating *lead-foil* with a little *iodine* in a test-tube. Separate the compound from excess of lead by means of boiling water. Compare the properties of the compound with those of the elements.

5. Examine the properties of iodine, i.e. solubility in water, alcohol, effect of heat in a bulb-tube.

Place a *small* drop of mercury in a mortar and add solid iodine and some alcohol. Grind the materials together, and if the iodine disappears add more. When iodine remains in excess after thorough grinding, add water, and wash out the contents of the mortar on to a filter-paper in a funnel, wash with alcohol, and dry at 110°C .

Draw up in parallel columns the properties of iodine, mercury, and mercury iodide, a compound of the two.

•

Compounds and Mixtures. These experiments will have shown that a profound difference exists between the properties of a mixture of iron and sulphur and the properties of a compound of the two elements.

The sulphur can be dissolved out from *the mixture* by carbon disulphide and the iron can be attracted by a magnet; they may easily be separated by winnowing, by shaking with water, by means of carbon disulphide, or a magnet; the addition of a small quantity of one or other of the elements does not appreciably alter the properties of the mixture.

In the *compound*, on the other hand, the sulphur will not dissolve, a magnet has little or no effect, so that the presence of iron and sulphur cannot be detected by these tests; the elements cannot be separated by the mechanical means which were effectual in the case of the mixture; the proportion by weight of iron to sulphur is fixed and cannot be altered.

Similar experiments with other substances show that their compounds differ very widely from their mixtures, even when the weights of the substances are the same in both.

It is generally supposed that this remarkable difference is due to the fact that, in the compound, the components are held together by a force known as **chemical affinity**, whereas, in the case of a mixture, this force has not been brought into play.

The characteristic properties of an element are completely hidden as soon as it has entered into combination with another, under the influence of this force. The compound formed has a definite gravimetric composition and characteristic properties which bear little or no resemblance to those of the elements it contains.

The components of a mixture can be separated from one another by making use of individual properties such as solubility, melting-point, boiling-point, density, &c., whereas the constituents of a compound cannot be separated in these ways.

Mechanical and physical methods for separating the components of a mixture. As most natural materials consist of mixtures, it is of importance in many industries, e.g. mining, to separate them in order to obtain one or more components free from the others. Many metallic ores, for example, consist of the metallic compound mixed with stone, and it is necessary to get rid of the stone before the smelting of the metallic compound is attempted. Very many methods of separation are in use, and the following list only gives a few, most of which have been met with in previous chapters :—

I. FOR MIXTURES OF SOLIDS.

- (a) *By taking advantage of the differences in density* of the components of the powdered mixture, as in winnowing, sifting, shaking with a liquid to let one component float while the rest sinks, as in Exp. 1, p. 149, where sulphur and iron were separated.
- (b) *By melting one component* and allowing it to flow away from the infusible matter, e.g. the separation of sulphur from admixture with stone.
- (c) *By volatilization of one component* by heating the mixture, e.g. as sal-ammoniac can be separated from non-volatile salt (see Problem 4, p. 52).
- (d) *By solution of one or more components*, e.g. the separation of gunpowder into nitre, sulphur, and charcoal by means of water and carbon disulphide (see Problem 9, p. 131).

II. FOR MIXTURES OF LIQUIDS AND SOLUTIONS.

- (a) *By distillation.* For example, sea water can be separated into sea-salt and pure water (see p. 33).
- (b) *By fractional distillation*, the liquid distilling over at low temperatures being collected in a different vessel to that obtained at higher temperatures, e.g. the separation of alcohol from admixture with water (see p. 37).

III. FOR MIXTURES OF GASES.

- (a) *By solution of one component*, e.g. a mixture of oxygen and sulphur dioxide could be separated by shaking with water. The former remains gaseous while the latter dissolves. On heating the solution the sulphur dioxide is expelled and can be collected as a gas again.
- (b) *By diffusion* through unglazed porous tubes, if the densities of the components are not nearly equal (see p. 207).
- (c) *By liquefaction* and subsequent evaporation. A mixture gives off gases of different densities, but the gas from a compound has the same density whether it be the first portion or the last.

Air a mixture of gases, not a compound. Air is principally made up of nitrogen and oxygen. It is considered to be a mixture and not a compound of these gases for the following reasons:—

(1) If artificial nitrogen and oxygen are mixed in the proportions in which they are found in air there is no change in temperature (as would occur if they combined), and the mixture cannot be distinguished from air which has been freed from the small quantities of other gases which it contains.

(2) If air be shaken up with pure recently-boiled water, some dissolves. On extracting this and treating it as in Exp. 6, p. 111, the volume of oxygen is found to be 36 %, while that of ordinary air is 21 %. Oxygen is known to be more soluble in water than nitrogen; hence each gas has dissolved in accordance with its own solubility and partial pressure. The composition of that which dissolved would have been the same as ordinary air in the case of a compound.

(3) On liquefaction and subsequent evaporation the nitrogen passes off first, leaving the oxygen (see p. 109).

(4) The density of air—neglecting small quantities of gases

other than nitrogen and oxygen—is the mean of the densities of nitrogen and oxygen when calculated with regard to the volumetric proportions in which they occur in air; e.g. the density of nitrogen is 14, and of oxygen 16. Taking air as consisting of $\frac{4}{5}$ nitrogen and $\frac{1}{5}$ oxygen by volume, the density of air should be $\frac{4}{5} \times 14 + \frac{1}{5} \times 16 = \frac{72}{5} = 14.4$. This is approximately identical with the density of air obtained experimentally.

Problems on separation of mixtures. 1. Find the percentage of salt in the given mixture (salt and sal-ammoniac), the other component being volatile. Use about 2 g. of the mixture.

2. Obtain a specimen of alcohol which will burn from the given mixture of alcohol and water. B.P. of alcohol is 79° C. and of water 100° C. Submit your plan for approval before beginning.

3. Separate the given mixture of sand and salt without losing any of either component. Submit your method for approval.

Physical and chemical changes. The changes to which single substances* (i. e. elements and compounds) are liable may be broadly divided into groups, viz.:—

I. Those changes in which there is no evidence of the production of a fresh substance (Physical Changes).

II. Changes in which one or more fresh substances are undoubtedly formed (Chemical Changes).

As a typical example of the first group, consider the changes which take place during the conversion of a lump of ice into steam. The ice, which is hard, brittle, of definite shape, and which has other properties associated with the term 'solid', is transformed by heat into water. Water, being fluid, has no definite shape, and has the other general properties of a liquid. On further heating, this liquid alters in volume, in density, in temperature, and is finally converted into steam. Steam, at high temperatures, behaves like a gas with regard to the laws

* The term 'single substance' will be used to include elements and compounds, but to exclude mixtures. Chemistry chiefly deals with the two former groups. Mixtures are used as a source for obtaining single substances, but are beyond the scope of strictly chemical investigation.

of Boyle and Charles, and, compared with water, has a very low density. Thus, during the transformation of ice into water, and water into steam, a great many alterations in properties can be observed, but the *matter* of steam is recognized as being the same as that of water and ice: they are not regarded as entirely different substances. On cooling the steam, water, and finally ice, may be re-formed.

Changes such as these are called *Physical Changes*. Change of state, such as is brought about by the solvent action of a liquid on a solid, is also regarded as belonging to this class, provided that the *original* solid can be recovered by evaporation of the solution.

As an example of the second group take the action of heat on magnesium in air. Here a tough lustrous metal and an invisible gas unite to form a white friable powder. On cooling, the original substances are not re-formed, nor is it possible to obtain either of them from the white powder by the action of heat alone. Again, when the red crystalline powder known as mercury oxide is heated, a colourless *gas* and a bright metallic *liquid* are obtained, both of which have properties totally different from the original red *solid*. Such are examples of *Chemical Change*.

On comparing the two types, physical changes are seen to be the simplest, for chemical changes always involve more than one substance, all of which may undergo a preliminary or subsequent physical change. The only real distinction between the two depends on whether there is, or is not, any evidence of the production of a fresh substance during the change. If there is, the change is chemical; if not, it is merely physical.

Both types have one feature in common, namely, *the total mass* of the material subjected to either kind of change remains unaltered.

One gram of ice yields exactly one gram of water or one gram of steam; and one gram of magnesium oxide is made from 0.6 g. of magnesium and 0.4 g. of oxygen.

Relation of physics to chemistry. *Physics* is the branch of Natural Science which deals principally with those properties, and changes in properties, of materials that involve no alteration in composition; it is subdivided into Heat, Light, Sound, Magnetism, Electricity, &c. The study of the thermal, optical, magnetic, and electrical properties of materials is the subject-matter of Physics.

Chemistry is the branch of science which studies changes in composition, i.e. the production of new substances from others—and changes in properties which accompany such changes in composition.

Since bodies are recognized by their physical as well as by their chemical properties, a knowledge of the former is essential for a thorough understanding of chemistry. Thus the two branches are intimately connected and the distinction between them is primarily a matter of convenience.

Kinds of chemical change. The simplest chemical changes can be divided into two classes, viz.:—

1. *Combination or synthetical change*, in which two substances unite to produce a third; e.g. magnesium and oxygen combine to form magnesium oxide.

2. *Decomposition or analytical change*, in which one substance forms two different substances; e.g. mercury oxide, on heating, yields mercury and oxygen.

There are several other kinds of chemical change besides these; they will be noticed later on.

Conditions of chemical change. There has been abundant evidence in several experiments to show that before a chemical change can occur certain physical conditions must be fulfilled. For instance, before mercury oxide can be decomposed it must be raised to a *certain temperature*, otherwise the change does not occur. When two substances react chemically they must be *in contact*; the greater the surface of contact the more rapidly does the change occur. The presence of a third substance is necessary when the two reacting bodies are solid and do not

easily melt. For example, dry carbonate of soda does not act on dry tartaric acid,* but when water is added an action occurs due to the fact that it dissolves some of each and brings them into sufficiently close contact for the change to take place.

Definitions. It is impossible to acquire clear ideas about any subject without having clear notions of the meaning of the terms used to describe it. It is therefore necessary to attach a definite meaning to a given word or phrase to avoid confusion. At the same time, it is often difficult to draw up rigorous definitions so as to include *all* cases which are recognized as being covered by a term and to exclude *all* others. This difficulty is especially prominent in chemistry, as new discoveries are constantly being made, with the result that the line of demarcation between terms becomes less distinct, and their re-definition does not keep pace with discovery.

The following are given as being useful when broadly employed, but they must not be pushed too far:—

Physical change *involves an alteration in the properties of substances, no new substance being formed.*

Chemical change *involves the formation of a fresh substance or substances differing widely from the original in essential properties.*

An element *is a substance incapable of decomposition into simpler substances by any known means.*

A mechanical mixture—

(i) *is, usually, capable of separation into its component substances by mechanical or physical means;†*

(ii) *exhibits most of the characteristic properties of each component;*

(iii) *does not appreciably alter in properties if the proportion of the components is slightly varied.*

* Used in making aerated water in a seltzogene.

† i.e. any method which does not call the force of chemical affinity into play, such as those mentioned on pp. 152–154.

A chemical compound—

- (i) *cannot, usually, be separated into its constituents by mechanical or physical means ;**
- (ii) *does not exhibit the characteristic properties of its constituents ;*
- (iii) *contains the constituents in a fixed proportion by weight.*

QUESTIONS ON CHAPTER X.

1. What is a chemical element? Give four examples of each of the two classes into which elements are divided. Mention the chief differences in the leading properties of the two classes.
2. Describe experiments to show the differences between a mixture and a compound of the same two elements.
3. Classify the following as elements, compounds, or mixtures, giving concise reasons in each case :—magnesium oxide, charcoal, air, mercury, methylated spirit, sea water.
4. Indicate the lines on which you would proceed to discover whether a given substance was an element or a compound.
5. Define the terms *compound* and *mixture*, and illustrate each point of your definition by two good examples.
6. Describe, in detail, physical or mechanical means that could be employed to separate the following mixtures :—(a) Powdered charcoal and copper oxide ; (b) sulphur and sand ; (c) alcohol and water ; (d) a solution of blue vitriol ; (e) oxygen and sulphur dioxide ; (f) iodine and graphite (black-lead).
7. Give reasons for considering gunpowder to be a mixture and not a compound of nitre, sulphur, and charcoal.
8. State, giving concise reasons, whether the following involve chemical or physical changes :—(a) the rusting of iron ; (b) the burning of coal-gas ; (c) the distillation of sea water ; (d) the action of heat on iodine ; (e) the action of heat on wax ; (f) the solution of salt in water.
9. Describe the changes which occur when crystals of blue vitriol are heated. Discuss the question whether they are physical or chemical.
10. When magnesium ribbon is gently warmed in air certain

* See note † on previous page.

changes occur while heat is being received ; at a certain temperature no more external heat is required, and both heat and light are produced by the burning ribbon. Describe these changes in detail, stating which are physical and which chemical.

11. Name three chemical changes during which heat is produced, and three in which heat is absorbed.

12. On what grounds is air considered to be a mixture, and not a compound of nitrogen and oxygen ?

13. Explain the terms *synthesis* and *analysis* as used in chemistry. Name two synthetical changes and two analytical changes.

14. Trace the changes undergone by the solid wax of a burning candle, distinguishing the physical from the chemical changes.

15. Define the terms *physical change* and *chemical change*, and give two good examples in each case so as to bear out each point of your definition.

16. Illustrate, by means of various examples, the statement that the conditions favourable to the production of chemical change are not necessarily the same in all cases.

CHAPTER XI

OXIDES, ACIDS, ALKALIS, SALTS

Preliminary Questions on Oxides.

1. DRAW up a list (in tabular form) of all the oxides you have made. State briefly, in each case,—

(a) How it was made.

(b) What elements it contains.

(c) Its physical state.

(d) Colour.

(e) Any other striking properties, especially those which enable you to distinguish it from others.

2. State concisely why you consider an oxide—say magnesium oxide—to be a compound and neither an element nor a mixture.

3. How would you define the term 'oxide' so as to *include* all those in your list, but to *exclude* other substances (e.g. nitre and potassium chlorate) which, although they contain oxygen, are not oxides?

4. What evidence was found in Chap. IX pointing to the possibility of water being an oxide?

Oxides, oxidation, and reduction. An oxide is a compound of oxygen with one other element. Substances like potassium chlorate and nitre are not oxides since they can be shown to contain *two* elements besides oxygen. The process of making an oxide from its elements, e.g. the formation of magnesium oxide by burning magnesium in air, is an example of a chemical change called oxidation.

Oxidation (*in the simplest sense*) is a chemical change in which the percentage weight of oxygen is greater in the new product than in the original substance. For example, the percentage of oxygen in the original magnesium is 0, but in the oxide it is 40. Again, when baryta (monoxide of barium) is heated in air barium dioxide is formed. This also is a case of oxidation, for the percentage of oxygen in the new product is 19, while it is only 10.4 % in the original baryta.

The reverse of oxidation is reduction of which the following examples have been met with:—the reduction of mercury oxide to mercury; of red lead to litharge (a lower oxide of lead); of barium dioxide to baryta (barium monoxide). These were all the result by the action of heat, and oxygen gas was evolved in each case.

Reduction (*in the simplest sense*) is a chemical change in which the percentage weight of oxygen is less in the new product than in the original substance. It was noticed that some substances in combining with oxygen do so with greater energy than others; e.g. magnesium on burning was oxidized completely, while lead only oxidized on the surface and did not emit light or any great amount of heat. It seems likely that if magnesium were heated with lead oxide the former would take the oxygen from the latter. In other words, the lead oxide would be reduced to lead and the magnesium oxidized to magnesia. This, in fact, does occur, and the magnesium plays the part of a *reducing agent*. It is also clear that in the exchange of oxygen between the two metals, oxidation and reduction go on simultaneously. From the point of view of the magnesium the change is one of oxidation, but from

the point of view of the lead oxide it is a case of reduction. Except in the simple combination of an element with oxygen and in the simple decomposition of an oxide by heat, oxidation and reduction always proceed simultaneously or, in other words, they are two ways of regarding the same chemical change.

Is water an oxide? In Exps. 3 and 4, pp. 121-3, the conclusion was drawn that water might possibly be an oxide of some substance. We know that water does not decompose on heating: it forms steam which on cooling condenses to liquid water again. It is important to try to settle this question and an attempt may be made by finding whether magnesium will act on it. If it does, and if water is an oxide, there ought to be no difficulty in recognizing the magnesium oxide, and the unknown substance in the water ought to be liberated, like lead from lead oxide. If no action occurs, then some other element which combines vigorously with oxygen must be tried.

Exp. I. To find whether magnesium will reduce water.

Required:—As in Fig. 47; test-tubes, emery-paper.

DIRECTIONS. *A.* Clean a strip of magnesium ribbon with emery-paper and put it into a test-tube half filled with water; boil the water and **note** whether any change takes place after standing for a time.

B. Clean 15 cm. of magnesium ribbon, roll it into a spiral and push it into the wide tube *T* (Fig. 47).

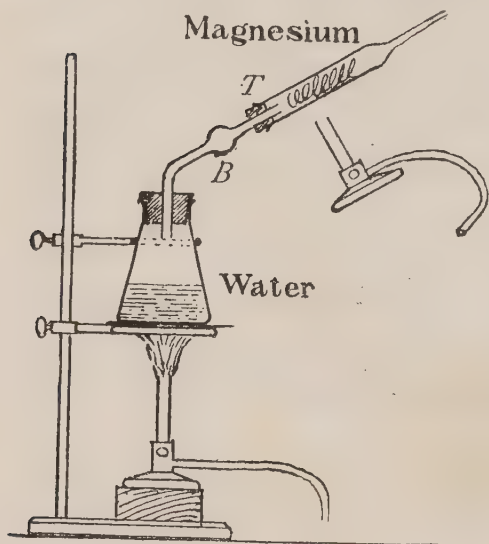


FIG. 47.

Fix up the rest of the apparatus as shown in Fig. 47.

(The small bulb *B* in the exit-tube is to prevent drops of water from entering *T*.)

Heat the water in the flask with a small flame, and at the same time keep *T* hot, by moving the other flame backwards and for-

wards along its whole length, to prevent the steam from condensing.

As soon as a rapid current of steam escapes, heat the magnesium strongly, until it begins to glow; then stop heating and hold the flame at the open end of the tube for a moment, leaving the action to complete itself. **Note** what happens.

LABORATORY RECORD. Diagram and observations.

Questions:—(i) Has magnesium an action on boiling water?

(ii) Did any visible action take place in *T* before the magnesium was red-hot?

(iii) What change did the magnesium in *T* finally undergo?

(iv) What happened to the steam? Explain how it was changed, and state what you conclude about the products.

(v) Give reasons for supposing that a *chemical* change has taken place between steam and magnesium.

Exp. 2. To investigate the action of boiling water and superheated steam on iron.

Required:—As in Fig. 48; clean iron filings, 2 burners, gauze.

DIRECTIONS. *A.* Find out whether there is any apparent change when iron filings are boiled with water.

B. Use the apparatus shown in Fig. 48. Carefully heat the tube *T* (over which wire gauze has been wrapped) so as to prevent the condensation of steam in it. Heat the flask until the water boils quietly and all air has been driven out of the apparatus. Then heat *T* strongly

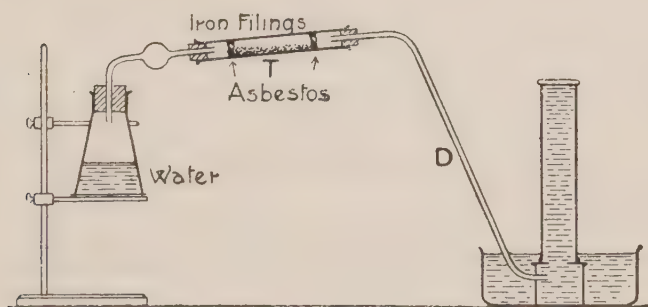


FIG. 48.

and collect the gas which escapes by placing the end of *D* under an inverted jar filled with water. Test the gas, and when *T* is cold turn out its contents on to a piece of paper and compare them with some of the original filings and the substance formed by burning iron in oxygen (p. 106).

LABORATORY RECORD. Diagram of apparatus and observations.

Questions:—(i) Has pure water any action with iron filings (*a*) at the air temperature, (*b*) at $100^{\circ}\text{C}.$?

(ii) Was there any apparent action between iron and steam, at any temperature below red heat?

(iii) Does the gas resemble that obtained in Exp. 1 or not?

(iv) How does the residue in *T* differ in appearance from the filings?

(v) What do you think is formed when the gas burns in air?

The reduction product of water. Experiments 1 and 2 have shown that an inflammable gas is formed when magnesium and iron are heated in steam together with *one* solid in each case, which is recognized as an oxide of the metal. The conclusion drawn from Exp. 4, p. 123, has been confirmed, viz. that *water is an oxide*, and it has now been found to be the oxide of a colourless inflammable gas. This gas, formerly known as inflammable air, is called *hydrogen*. It is an element, and will be prepared on a larger scale in Chapter XIII. It is important to grasp firmly what has already been proved about these simple compounds by expressing the facts as follows:—

Magnesium + oxygen yield magnesium oxide. (I)

Magnesium + steam yield magnesium oxide + hydrogen. (II)

∴ Steam (or water) is oxide of hydrogen. (III)

Other evidence confirming III will be met with later on.

Exp. 3. To observe the action of water and litmus on some common oxides.

Required:—Oxides of magnesium, lead, zinc, copper, iron, phosphorus; purple litmus solution, porcelain basins, glass rods, balance, desiccator, carbon, sulphur, oxygen.

DIRECTIONS. **Note** the obvious properties of each solid oxide and **record** them, arranged as below.

A. Put a little of each solid (except oxide of phosphorus) on a separate red litmus-paper, add *one* drop of water, and make into a paste with a glass rod.

Rinse off the solid by dipping the paper in a dish of distilled water **Note** any colour change.

Remove a little oxide of phosphorus from a bottle with a dry glass rod and place it in a basin containing a few drops of water. Dip a piece of (a) red, (b) blue litmus-paper into it. **Note** any colour change.

[Litmus is a complex vegetable colouring matter; its use in chemistry is shown in this and the following experiments.]

B. Take two jars of oxygen and make oxides of carbon and sulphur as on p. 105. Add litmus solution and shake.

Note any colour change.

C. Find whether pure water affects the colour of purple litmus.

D. Weigh a small porcelain basin. Add about 1 gram of phosphoric oxide* and reweigh quickly. *Very carefully* add a few drops of water. Evaporate over a sand-bath, until no further alteration seems to occur. Cool in a desiccator and weigh again.

Note whether there is an alteration in weight and whether the residual substance is similar or dissimilar to the original oxide in its obvious properties.

LABORATORY RECORD. Tabulate observations thus:—

Name of oxide		
Colour and physical state . .		
Action on moist litmus-paper .		
Whether deliquescent . . .		
Other properties observed . .		

Record of weighings in D.

* Should be free from lower oxides of phosphorus.

Exp. 4. To make the oxides of sodium and calcium and to observe their action on water.

Required:—Oxygen, 2 gas-jars and cover-plates, deflagrating spoon, sodium, calcium, litmus, 2 porcelain basins.

DIRECTIONS. *A.* Examine the sodium kept in a bottle of petrol.

[It is a metallic element obtained from common salt and is contained in caustic soda, washing soda, &c. Since it is rapidly acted on by moist air it is kept under oil.]

Take out a small piece and press it between filter-papers to remove the oil. Scrape it with a knife, cut off and examine a piece about the size of a pea. Place it on a *clean* deflagrating spoon and heat in a flame.

Precaution. *Hold the spoon well away from your face, and avoid letting water touch the sodium.*

When hot place it in a dry jar of oxygen and **note** what happens.

After cooling scrape out the residue into a dry dish and add a little water. **Note** whether it dissolves or not.

Test the liquid with red and blue litmus-paper and **observe** any change in colour.

B. Clean out the spoon and repeat *A*, using a small piece of calcium,* but heat much more strongly—until the spoon is bright red.

After adding water and testing with litmus-paper, pour the liquid and undissolved solid into a small flask, shake well and filter.

Dip a glass tube into the clear filtrate and breathe through it.

Note whether any change takes place in the liquid.

LABORATORY RECORD. Description of properties of sodium and calcium. Tabulate properties of the oxides as in Exp. 3.

* Fragments of calcium may be kept imbedded in paraffin wax; when required for use, the paraffin may be melted off and the fragments cleaned by washing with petrol.

- Questions*:—(i) Which oxides used in Exps. 3 and 4 are quite insoluble and without effect on litmus?
- (ii) Which form *acid* solutions and redden the litmus?
- (iii) Which form *alkaline* solutions and turn litmus blue?
- (iv) Is the residue obtained by evaporating a solution of oxide of phosphorus identical with the oxide or not? Give reasons for your conclusion.
- (v) Is the action of water on phosphorus oxide a physical or a chemical change? Give a reason.
- (vi) What other solution behaves like a solution of calcium oxide on breathing into it?
- (vii) Is there any difference between solutions of the oxides of (a) metals, (b) non-metals, with respect to litmus?

Exp. 5. To examine the action of water on lime.

Required:—*Quicklime, litmus, filter-papers, funnel, 2 small basins, thermometer, test-tubes, balance.*

DIRECTIONS. Put into each of two basins three pieces of quicklime.*

A. To one add water, drop by drop, until no more is absorbed.

Note what happens and whether the temperature alters.

After 10 minutes take a little of the solid (called slaked lime) from the dish and shake with water in a test-tube; filter and divide the filtrate into two portions, *X* and *Y*.

Note the effect of adding litmus to *X* and of breathing through *Y*.

B. Whilst *A* is proceeding weigh the other dish. Add distilled water, drop by drop, until the lime is moist. When all action has ceased, place the basin in an air oven not above 120° C. to dry the solid. Reweigh when cold.

LABORATORY RECORD. Observations in *A*; weighings in *B*.

* Quicklime is made by heating limestone to a high temperature in kilns. If possible, the quicklime should be previously heated to a high temperature in a muffle furnace before use.

[Over.]

- Questions :—**(i) Does slaked lime weigh the same as the lime used to make it?
- (ii) Which is the more complex, quicklime or slaked lime?
- (iii) Compare the action of solutions of slaked lime and oxide of calcium on (a) litmus, and (b) carbon dioxide.
- (iv) Is lime an oxide of metal? Give reasons.
- (v) Is the action of water on quicklime a chemical or a physical change? Quote evidence for your conclusion.
- (vi) Is slaked lime a compound or a mixture?

PROBLEM (XI. 5). Find whether slaked lime can be converted to quicklime by the action of heat. Identify whatever you obtain.

The use of litmus. Litmus is one of many colouring matters which may be used to indicate the presence of acids. Any liquid, or solution, capable of turning purple or neutral litmus red, is said to have an *acid reaction*; similarly, one which turns it blue is said to have an *alkaline reaction*.

Acids have been known from the earliest times and were recognized by their peculiar sour taste. They occur in plants and especially in unripe fruits. Oxalic acid occurs in wood sorrel; citric acid in lemons; malic acid in apples; tartaric acid in grapes; formic acid in the stings of nettles and in ants. Many are produced artificially, e.g. vinegar or acetic acid by exposing wine to air, lactic acid by exposing milk to air. These all turn litmus red, and this is a safer and more convenient test than tasting.

Action of water on oxides. Experiments 3, 4, and 5 have shown that water has :—

- (1) no apparent action on some oxides, e.g. copper oxide;
- (2) a slight chemical action on some, detected by litmus, e.g. lead and magnesium oxides;
- (3) a vigorous chemical action on others, forming new substances heavier than the original oxides and therefore compounds, e.g. phosphoric oxide and calcium oxide (lime).

*An **alkaline oxide** is an oxide which combines with water to form an alkali.*

Since alkalis contain a metal combined with hydrogen and oxygen their composition is expressed by naming them after the metal with the word *hydroxide* following; thus, slaked lime is called *calcium hydroxide* (or calcium hydrate—but the former term is preferable). So also: sodium hydroxide, magnesium hydroxide, &c.

Common acids and alkalis. It must not be assumed that all acids are produced by the action of water on oxides; there are many which cannot be made in this way.

It is customary to classify acids broadly according to the source from which they are derived, viz.:—**mineral acids**, obtained partly from minerals or inorganic materials, and **organic acids**, obtained from vegetable or animal products. Sulphuric, hydrochloric, and nitric acids are the most important mineral acids, and acetic, tartaric, and oxalic acids are among the most common organic acids.

The **principal alkalis** are caustic soda or sodium hydroxide, slaked lime, and caustic potash or potassium hydroxide. The last-named can be made from potassium oxide and water, and is a solid very similar to sodium hydroxide in its general physical and chemical properties.

Exp. 6. To examine the obvious properties of the caustic alkalis.

Required:—Caustic soda, caustic potash, platinum wire, dishes.

DIRECTIONS. Examine each solid and **note** (*a*) colour, (*b*) whether deliquescent or not, (*c*) whether soluble in water, (*d*) action of litmus, (*e*) flame coloration (see p. 137), (*f*) effect of touching them with the fingers.

LABORATORY RECORD. Observations, neatly arranged.

Questions:—(i) How can caustic soda be distinguished from caustic potash?

(ii) How can both of these be distinguished from slaked lime?

Sodium and potassium hydroxides are also known as caustic soda and caustic potash respectively, owing to their action on skin which they are capable of dissolving with a burning or caustic sensation. They are not usually made in a laboratory, but are manufactured on the large scale by various processes of a complex nature. They can, however, be made from their metals by oxidation and subsequent combination with water as was done in Exp. 4, p. 168.

The oxides of sodium and potassium combine with water to form the hydroxides of these metals, just like lime (calcium oxide) combined with water yielding calcium hydroxide (or slaked lime) in Exp. 5, p. 169. In each case the hydroxide weighs more than the oxide by the weight of water which has entered into combination. On strongly heating calcium hydroxide (and most other hydroxides) water is given off and the metallic oxides remain. This does not apply, however, to potassium and sodium hydroxides—they are not decomposed by heating in a Bunsen flame.

Exp. 7. To observe the action of sodium on water.

Required:—Sodium, 'compo.' tubing, litmus-paper, large and small porcelain basin, gas-jar, glass plate.

DIRECTIONS.—*A* Press a piece of sodium (about the size of a small bean) between folds of filter-paper. When free from oil, cut it into small pieces. Drop one of these into a little water, contained in a small basin, and cover the basin with a glass plate.

Note what happens (*a*) to the sodium, (*b*) to a piece of red litmus-paper placed in the water.

When the action is over, add another piece of sodium, and so on; until all have been put into the water. Evaporate the residual liquid to dryness on a sand-bath.

After B has been done, examine the contents of the basin.

B. Place a small piece of sodium in a small piece of 'compo.' tubing closed at one end, and put it under the mouth of an inverted gas-jar, full of water, standing in a basin.

Find whether the gas obtained will burn and so identify it.

LABORATORY RECORD. Description of *A* and *B*. Diagram for *B*.
Questions:—(i) Why is sodium preserved under oil?

(ii) How did you identify the solid left in *A*?

(iii) How did you identify the gas?

(iv) Name both products and state what happens to the solid when exposed to air.

PROBLEMS (XI. 7). 1. Repeat Exp. 7 *A* with *potassium*, observing the action through a sheet of glass placed over the basin.

2. Investigate the action of metallic *calcium* on water, and prepare a specimen of the product of the action.

Exp. 8. To compare some properties of sulphurous and sulphuric acids.

Required:—Syphon (or other supply) of sulphur dioxide, small flask, 2 basins, test-tubes

PRELIMINARY NOTE. Sulphuric acid was formerly obtained by distilling green vitriol crystals. Being a thick, viscous liquid it was called 'oil of vitriol', which was known and used long before its chemistry was understood. It is one of the most important chemicals, since by its interactions large numbers of fresh substances can be made. It will be useful to know enough to be able to recognize it in the future.

The composition of sulphurous acid, on the other hand, has already been ascertained, but the facts may be recalled to fix them firmly in the memory:—

Sulphur + oxygen yield sulphur dioxide.

Sulphur dioxide + hydrogen oxide yield sulphurous acid.
(water)

∴ Sulphurous acid contains $\left\{ \begin{array}{l} \text{hydrogen} \\ \text{sulphur} \\ \text{oxygen} \end{array} \right. \left\{ \begin{array}{l} (a) \text{ from sulphur dioxide. (VI)} \\ (b) \text{ ,, hydrogen oxide.} \end{array} \right.$

This acid cannot be separated from the excess of water in which it is formed by the solution of sulphur dioxide—it exists only in solution and has not been isolated.

DIRECTIONS. *A.* Put 20 c.c. of water in a small flask and pass sulphur dioxide into it until, after shaking the water in the flask, it smells strongly of the gas. This is a solution of sulphurous acid.

B. Evaporate about 5 c.c. in a basin in a draught chamber and **note** what happens. Before the liquid has all disappeared put a drop on to a piece of paper and warm it gently over a flame.

C. To a few drops of the acid in a test-tube add two drops of chromic acid solution. **Note** the effect.

[Over.

- D.* Repeat *B* and *C* with diluted sulphuric acid taken from a bottle. **Note** results.
- E.* Try the effect of putting *one* drop of *concentrated* sulphuric acid on a piece of paper. **Record** result.
- F.* Compare the action of barium chloride solution on a few drops of sulphurous and dilute sulphuric acids. Then add a little hydrochloric acid in each case. **Note** any differences in behaviour.

LABORATORY RECORD. List of observations, neatly arranged.

- Questions :—(i) Name as many similarities as you can between the two diluted acids.
- (ii) By what tests may the two acids be distinguished?

Exp. 9. To oxidize sulphurous acid with mercuric oxide.

Required:—Syphon of sulphur dioxide, gas-jar and cover, mercuric oxide, boiling-tube, filter, porcelain basin.

DIRECTIONS. *A.* Weigh out about 1 gram of mercuric oxide. Fill a gas-jar with sulphur dioxide by downward displacement of air, and put on a cover plate. Pour into the jar one test-tubeful of distilled water; put on the cover-plate and shake. Then add the mercuric oxide and shake until it is converted into a white solid. If some red oxide still remains, pass in a little more sulphur dioxide and shake again.

Transfer all the contents of the jar to a boiling-tube and heat until the liquid boils and the white solid has been converted to a black one.

Filter through two thicknesses of filter-paper into a porcelain dish. Test the filtrate with litmus-paper and barium chloride acidified with hydrochloric acid, and **note** the result. Dry the black solid in a steam-oven. Evaporate the remaining filtrate on a sand-bath till only three or four drops remain. Put a drop of the liquid on a piece of ordinary paper and hold it well above a flame for a short time. **Note** the result.

B. Examine the substance on the dried filter-paper and **note** its appearance and properties.

LABORATORY RECORD:—Observations in *A* and *B*.

- Questions:—**(i) What is the substance left on the dry filter-paper?
(ii) What is the liquid obtained on evaporation in *A*?
(iii) What has happened to the mercuric oxide (neglecting the formation of the intermediate white solid)?
(iv) Would you expect the anhydride of sulphuric acid to contain less or more oxygen than sulphurous anhydride (sulphur dioxide)? Give a reason.

Composition of sulphuric acid. Exp. 9 shows clearly that sulphuric acid may be obtained from sulphurous acid by oxidizing it with mercuric oxide. Since we know the composition of the last two substances a conclusion may be drawn about the composition of sulphuric acid.

The mercuric oxide decomposed and left mercury. Therefore, as no escape of oxygen was observed, its oxygen combined with the sulphurous acid and converted it to sulphuric acid, i. e.—

Sulphurous acid + mercuric oxide = sulphuric acid + mercury.

∴ Sulphuric acid contains all that sulphurous acid contains + extra oxygen.

i. e. *Sulphuric acid contains hydrogen, sulphur, and a large amount of oxygen.* (VII)

If the elements of water could be taken from sulphuric acid, it is reasonable to expect that the anhydride obtained would consist of a higher oxide of sulphur than the dioxide. Whether this can be done or not will be seen later.

Exp. 10. To examine the action of zinc on sulphuric acid.

Required:—2 test-tubes, cork, glass jet, small basin, ignition tube, porous tile, platinum wire, zinc-foil, methylated spirit, measuring jar, flask, solutions of cobalt nitrate and chromic acid.

DIRECTIONS. *A.* Fit an ordinary test-tube with a cork bored with one hole through which passes a short piece of glass tube drawn out to a jet above the cork. See that it is air-tight. Pour 50 c.c. of water into a measuring jar and then 5 c.c. of concentrated sulphuric acid.

[Cork up the rest of the acid in a flask for Exp. 11.]

Precaution:—*Sulphuric acid is a dangerous liquid which destroys skin and clothes.*

Note whether the mixture is warm or not.

Pour 5 c.c. of the mixture into the test-tube, put in a piece of zinc-foil (about 2 sq. in.), fix the jet in the mouth and **note** what happens.

Invert another test-tube over the jet to collect the gas evolved. Allow a little time for displacement of air, then close inverted tube with a thumb and bring it near a small flame, which should be a yard away.

Note whether the gas burns quietly. If not, try again.

Precaution:—*The generating tube must not be near a flame until the collected gas burns quietly.*

Find whether the gas will now burn at the jet. When effervescence slackens, remove the cork and heat by putting the tube in boiling water; if the metal has nearly all dissolved, add more.

When the action seems to be over, filter (using a *small* filter-paper) from excess of metal into another tube and allow to cool.

If no solid appears, shake the tube and, if necessary, add about 1 c.c. of methylated spirit (in which the solid is

less soluble than in water). **Note** the appearance of the solid.

B. Drain the crystals on a porous tile and gently heat a *portion* in an ignition tube (held with the mouth slightly sloping downwards), having placed a little blotting-paper moistened with chromic acid in the mouth.

Then heat more strongly. **Note** all that happens.

Test the residue left in the tube with cobalt nitrate (see p. 138) and so identify it.

Re-dissolve some of the crystals in water and test with barium chloride in presence of hydrochloric acid.

Note what happens.

LABORATORY RECORD. Diagram of apparatus used. Observations.

Questions:—(i) What gas was evolved?

(ii) Did the gas come from the acid or the water? Give a reason.

(iii) What has become of the zinc? Quote evidence.

(iv) What has become of the sulphur of the sulphuric acid? State evidence.

(v) What elements are contained in the solid after the water of crystallization is expelled?

(vi) What elements are contained in sulphuric acid?

(vii) What conclusion do you draw from the fact that barium chloride causes the precipitation of the same white solid when it reacts with (a) sulphuric acid as it does with (b) a solution of the crystals formed by the action of zinc on the acid?

(viii) Express the action of sulphuric acid on zinc in the form of a verbal equation as on p. 178.

Exp. 11. To examine the action of zinc oxide on sulphuric acid.

Required:—As in Exp. 10; pure zinc oxide (free from carbonate).

DIRECTIONS. Put about 5 c.c. of the diluted sulphuric acid made in Exp. 10 in a test-tube and add *pure* zinc oxide gradually until no more dissolves after warming in hot water. (Compare the action with that of zinc on the acid.)

Filter (using a *small* paper) and cool, adding a few drops of methylated spirit, if necessary, to bring down the solid.

Drain the crystals on a porous tile and test them as in Exp. 10, B.

LABORATORY RECORD. Careful observations.

Questions:—(i) Was any hydrogen evolved in the action?

(ii) What element is present in zinc oxide which is absent in metallic zinc?

(iii) Are the crystals obtained in Exps. 10 and 11 identical or not?

(iv) Account for the absence of effervescence in Exp. 11.

(v) Write a verbal equation to express the action of zinc oxide on sulphuric acid.

Salts. The solid substance obtained in Exps. 10 and 11 by the action of zinc and zinc oxide on sulphuric acid belongs to a class of chemicals called *salts*. This particular salt—zinc sulphate—is identical with *white vitriol*, which has long been known. It is necessary to have a clear idea of the composition of salts and of their relation to acids, since they form a very large class. If the previous experiments are regarded as typical, we have enough evidence to show what a salt really is.

Zinc + sulphuric acid gave hydrogen + zinc sulphate.

\therefore Zinc sulphate = sulphuric acid – hydrogen + zinc. (VIII)

or, in other words, zinc sulphate only differs from sulphuric acid in possessing zinc instead of hydrogen.

Taking this action as typical, it may be stated that—

a salt is derived from an acid by the substitution of a metal in place of hydrogen.

Further, the formation of the same salt by the action of zinc oxide on the acid may be presumed to be as follows:—

Zinc oxide + sulphuric acid = hydrogen oxide + zinc sulphate.

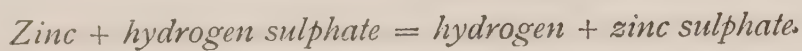
Actual proof of the formation of water is lacking, since the whole reaction was performed in presence of large excess of water. But since water is hydrogen oxide, and there is known to be oxygen in the zinc oxide and hydrogen in the acid, and as neither of these gases was given off, the above presumption is probable. [A proof will be given later on, p. 190.]

Another deduction can be made from conclusion VIII, viz. if zinc sulphate consists of the same elements as sulphuric acid, except that the zinc replaces hydrogen, then—

Sulphuric acid may be called hydrogen sulphate.

Substitution or replacement. The action of zinc on sulphuric acid belongs to a type of chemical change known as *substitution*. The two simplest types of change, viz. *combination* and *simple decomposition*, were defined on p. 157. Ob-

viously the action of zinc on sulphuric acid differs from *combination*, since there are *two* products of the change and not merely *one*. Thus:—



Substitution or replacement may be defined as a chemical change in which a free element displaces another element from a compound, replacing the latter and thereby forming a new compound. Thus, the free element zinc displaces hydrogen from hydrogen sulphate and replaces it, forming zinc sulphate while free hydrogen is liberated.

Double decomposition The action of zinc oxide on sulphuric acid does not belong to any of the types of chemical changes mentioned above. Here we have two *compounds* which react and produce *two* other compounds. Both of the original compounds are decomposed, and part of each one combines with a part of the other, forming two new compounds. Such a change is known as double decomposition.



The actions of barium chloride on sulphuric acid and on zinc sulphate are cases of double decomposition. Other examples will be noticed later.

Acid radicals. In considering the composition of an acid and its salts, we see that there is a portion of the acid common to the salts. For example, the sulphur and oxygen of sulphuric acid is also contained in zinc sulphate, barium sulphate, and in all sulphates. That portion of these compounds indicated by the word *sulphate* is called an acid radical. The same applies to other acids and their salts. Hence an acid radical is an element or group of elements which exist in an acid and in the salts derived from it.

QUESTIONS ON CHAPTER XI.

1. Distinguish between 'oxides' and other compounds which contain oxygen. Give examples.
2. Explain the terms *oxidation* and *reduction*, giving two examples of each type of action.
3. State the evidence for believing that water is composed of oxygen and hydrogen, and describe in detail one method for obtaining hydrogen from water.
4. Give a general account of the action of water on various oxides, with examples.
5. Mention two substances which only undergo a physical change when dissolved in water, and two which undergo a chemical change under like circumstances. Explain a method by which you could prove your statements to be correct.
6. Write a short account of the obvious properties of sodium. Explain how its oxide can be made, and state what happens when this oxide is dissolved in water.
7. How are slaked lime and lime-water made, starting with quicklime? Would slaked lime or quicklime be produced on evaporating lime-water at $100^{\circ}\text{C}.$? Give reasons for concluding that quicklime is a metallic oxide.
8. Define the terms *acidic oxide*, *alkaline oxide*, *alkali*. Give two examples of each.
9. How can sulphurous acid be made? Give all the tests you know by which it can be distinguished from sulphuric acid.
10. Explain clearly how to prove that sulphuric acid contains sulphur, hydrogen, and oxygen, and that it contains a greater proportion of oxygen than sulphurous acid.
11. How may hydrogen be obtained from sulphuric acid? Devise apparatus for making and collecting two or three litres of it.
12. Describe two ways in which zinc sulphate can be prepared. Give evidence that it contains zinc, sulphur, and oxygen.
13. Define the term *salt*. State three methods by which magnesium sulphate could be made, given sulphuric acid and the other necessary substances.
14. Explain the terms *substitution* and *double decomposition*, giving examples of each.

CHAPTER XII

FURTHER STUDY OF ACIDS, BASES, AND SALTS

Summary of conclusions drawn from Chapter XI. It is important that the deductions made from the experiments of Chap. XI should be borne in mind. Put briefly they are :—

(1) **Water is hydrogen oxide.**

(2) **Hydrogen oxide + acidic oxide yield an acid.**
(Chiefly non-metallic oxides)

(3) **Hydrogen oxide + alkaline oxide yield an alkali.**
(Certain metallic oxides)

(4) **A Salt is a solid formed by replacing the hydrogen of an acid by a metal.**

This replacement can be effected by the action of the acid on a metal or on a metallic oxide, and in other ways.

Exp. 1. To observe the action of sulphuric acid on common salt.

Required:—Burette, test-tubes, taper, litmus-paper, platinum wire, silver nitrate, and above materials.

DIRECTIONS. *A.* Run 2 c.c. of water from a burette into a test-tube and mark the level of water with a rubber band. Empty out all the water and pour in concentrated sulphuric acid up to the mark.

Weigh out 5 g. of common salt, add it gradually to the acid, and **observe** the effect.

Note the smell and colour (if any) of the gas, and find (a) the effect of moist air on it, by blowing over the mouth of the tube, (b) whether the gas is combustible or supports the combustion of a taper, (c) whether it is lighter or heavier than air, (d) whether it is soluble or insoluble in water, (e) its action on neutral litmus-paper.

[This gas is *hydrochloric acid* and was formerly called *muratic acid*, while its solution in water was known as *spirits of salt*.]

B. After all the salt has been put in the tube, heat in a draught-chamber until no more gas comes off. Allow it to cool. If the tube is damaged, break it and transfer the solid to another tube *half* full of water (not more). Warm until the solid dissolves. Let it cool and drain the crystals* on a porous tile.

Note their shape and compare it with that of a crystal of common salt (p. 31). Try their flame coloration (p. 137). Dissolve a little in water (use a test-tube) and add a few drops of barium chloride solution and then a few drops of hydrochloric acid. **Note** the result and draw a conclusion.

C. Drop a piece of zinc into a test-tube half full of hydro-

* If none form, evaporate the solution to half its volume and cool.

chloric acid solution taken from a bottle. **Note** and identify the gas evolved.

D. To half a tubeful of dilute hydrochloric acid solution add a few drops of silver nitrate solution. Expose the tube to bright sunlight, or let it stand for some time in the light. **Note** the effect.

E. Repeat *D* with a solution of common salt. **Note** the result, compare it with that of *D*, and draw a conclusion.

Questions:—(i) What metal does common salt contain?

(ii) What metal do the crystals in *B* contain?

(iii) Are the crystals in *B* identical with those of salt or not? If so, account for the action; if not, what do you expect them to contain?

(iv) Does the new acid contain hydrogen? Give evidence.

(v) To what class of substances do the crystals in *B* belong?

(vi) Write a verbal equation for the action in *A*.

(vii) Is the same solid produced by the action of silver nitrate on hydrochloric acid as on common salt? If so, what conclusion do you draw respecting the composition of the acid and the salt? If not, what difference did you observe?

(viii) To what types of chemical change do the actions of (*a*) zinc, (*b*) silver nitrate on hydrochloric acid belong?

Action of sulphuric acid on common salt. Exp. 1 has shown that there are two products of the action, viz. :—

- (a) *hydrochloric acid*, which was proved to contain hydrogen ;
- (b) a solid, proved to contain sodium and to be a sulphate, i. e. *sodium sulphate*.

The change is obviously one of double decomposition. The hydrogen of the sulphuric acid must have combined with part of the common salt to form hydrochloric acid, while the 'sulphate' part of sulphuric acid combined with the sodium of the common salt to form sodium sulphate.

The action of silver nitrate on hydrochloric acid and on common salt confirms this view, for the same solid was apparently formed in each case. These also appear to be cases of double decomposition ; hence, both the salt and the acid must contain something in common. This 'something' when in combination is expressed by the word *chloride*, common salt being sodium chloride and hydrochloric acid, hydrogen chloride. The action is represented thus :—



If this view is correct, sodium chloride (common salt) should be formed by neutralizing hydrochloric acid with sodium hydroxide. Evidence on this point will be gained in the next experiment.

Exp. 2. To examine the action of an acid on an alkali.

Required:—Hydrochloric acid, solid sodium hydroxide, small basin, lens, litmus-paper, small flask, glass rod, porous plate, platinum wire, silver nitrate.

DIRECTIONS. Dissolve about an inch of stick sodium hydroxide (caustic soda) in half a basinful of water.

Dilute about 25 c.c. of *pure* saturated hydrochloric acid solution in a flask with its own bulk of water.

Put a purple litmus-paper in the basin, and pour the acid gradually down a glass rod into the alkali, stirring frequently, until the litmus reassumes the neutral purple tint.

Evaporate to the crystallizing point over wire gauze. (If the liquid becomes alkaline during evaporation, add *very dilute* acid, drop by drop, till neutrality is restored.)

Allow it to cool; dry the crystals on a porous plate.

Examine the crystals with a lens and taste a small portion; find whether they contain water of crystallization. Test them for sodium and for a chloride.

Cork the remainder in a dry tube and label them, saying how they were obtained.

LABORATORY RECORD. Full observations.

Questions:—(i) What solid is formed? Quote evidence.

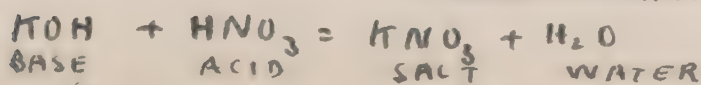
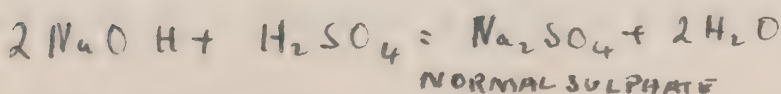
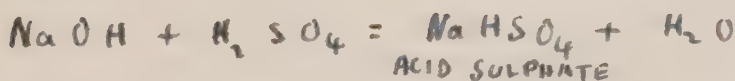
(ii) Is the change physical or chemical? Give a reason.

(iii) Is there any evidence of the production of more than one solid?

(iv) Write a verbal equation for the change. What type of change is it?

PROBLEMS (XII. 2). Perform similar experiments with:

1. Diluted sulphuric acid and sodium hydroxide solution.
2. Diluted *nitric acid* and *potassium hydroxide* solution.
3. Diluted hydrochloric acid and *solid slaked lime*.



Exp. 3. To examine the action of dry hydrochloric acid on copper oxide.

Required:—As in Fig. 49; dried copper oxide, boat, silver nitrate, white copper sulphate.

DIRECTIONS. Set up the apparatus shown in Fig. 49, using a *large* flask and taking care that the connexions are airtight.

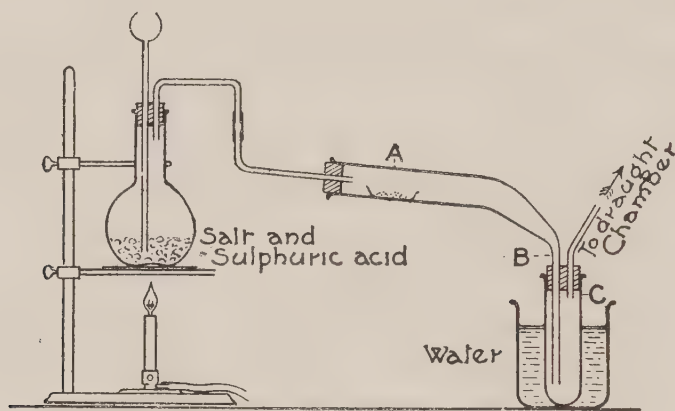


FIG. 49.

Detach the flask, and carefully slide salt into it so as to make a layer 1 inch deep.

Replace the cork carrying the tubes, and see that the end of the thistle funnel nearly touches the bottom of the flask, and that it is not choked with salt.

Fill a porcelain boat with *dried* copper oxide and place it in the tube A B (an 'adapter' bent for the purpose is suitable; the narrow part B should go nearly to the bottom of the test-tube).

Be careful not to spill any of the oxide out of the boat. The rest of the tube A B and the tube C must be clean and dry.

Cautiously pour concentrated sulphuric acid into the flask until it rises above the lower end of the funnel.

No heat is required at first, but a *small* flame may be put under the flask if the fuming hydrochloric acid gas ceases to

come out of the exit-tube from c in the draught-chamber. **Note** what happens at A; does it get hot? When a good deal of liquid has collected in A, warm it *gently* by rapidly moving a flame over it. Take care not to crack the tube by overheating. The liquid is thus driven down the slope into c. Continue to pass the gas over until the colour of the solid in the boat is uniform.

Take out the boat, dissolve a little of the solid in water, and test it with silver nitrate solution. **Note** the result.

Test the flame coloration of the solid, using the 'lead' of a pencil.

Examine the liquid in c (a) with neutral litmus-paper, (b) with white copper sulphate. **Note** the effects.

LABORATORY RECORD. Diagram of *actual* apparatus. Observations.

Questions:—(i) What is the (a) solid, (b) liquid product of the action?

(ii) Knowing that a large proportion of the hydrochloric acid gas could not touch the copper oxide and therefore could not act on it, but would pass through c, do you expect the liquid in c to be pure?

(iii) What has become of (a) the hydrogen, (b) the other part of the hydrochloric acid, (c) the oxygen, (d) the copper of the copper oxide?

(iv) To what class of chemicals does the brown solid belong?

(v) Write verbal equations for the action of (a) sulphuric acid on salt, (b) hydrochloric acid on copper oxide.

Basic oxides. In Exp. 2 the action of an anhydrous acid (i. e. an acid unmixed with water) on an insoluble metallic oxide was observed. On p. 182 the conclusion was drawn that the action of diluted sulphuric acid on zinc oxide resulted in the formation of a salt (zinc sulphate) and probably also of water. Owing, however, to the acid being dilute, no proof of the formation of *water* was obtained. The last experiment (p. 191) gives actual demonstration of the formation of water—



Any substance which reacts with an acid yielding a salt and water is called a **base**, and when the substance is an oxide it is called a **basic oxide**. Taking the action of black copper oxide on hydrochloric acid as typical of the action of basic oxides on acids, the conclusion may be drawn that—

A **basic oxide** + an **acid** yield a **salt** + **water**.

The alkaline oxides, such as the oxides of calcium (lime), sodium, and potassium, are basic oxides. They happen to be able to combine with water, forming hydroxides (alkalis), while the majority of basic oxides (e. g. copper oxide) do not combine directly with water. The hydroxides of metals possessing insoluble basic oxides can be made in other ways as in the next experiment.

Exp. 4. To prepare insoluble hydroxides of metals.

Required:—Solutions of lead nitrate and sodium hydroxide, small beaker, glass rod, filter, basins.

DIRECTIONS. *A.* Fill a quarter of a small beaker with a solution of lead nitrate, and pour a *strong* solution of sodium hydroxide into it down a glass rod until the mixture is alkaline.

Wash the precipitate by decantation, i. e. allow the solid to settle and pour away as much of the clear liquid as possible. Then add distilled water, stir well, allow to settle, and decant. Repeat two or three times.

Finally stir up with hot water and pour the whole contents of the beaker on to a filter.

Test a drop of the filtrate for sodium (see p. 137), and wash on the filter with hot water until all sodium compounds have been removed.

Carefully take the paper and solid out of the funnel and place in a porcelain dish, tearing off any superfluous paper. Spread it out with a glass rod and dry in an air-oven at 110°C .

B. Heat some of the dry solid in an ignition tube and **note** what happens; **identify** the solid by its colour and the liquid with white copper sulphate.

C. To a *few* drops of diluted nitric acid add some of the solid until no more dissolves. Filter into another basin; evaporate to crystallizing point. Heat the crystals in an ignition tube, and compare the result with the effect of heating a little solid lead nitrate.

LABORATORY RECORD. Full observations in *A*, *B*, and *C*.

Questions:—(i) What elements did the precipitate contain?

(ii) Express the action of heat on it by a verbal equation.

(iii) What substance (or substances) would be obtained by evaporating the clear liquid which was decanted in *A*?

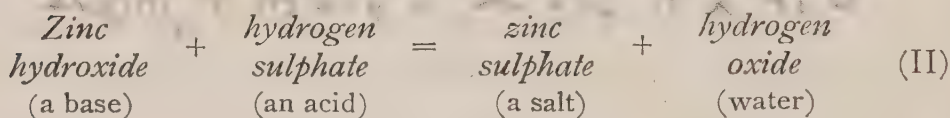
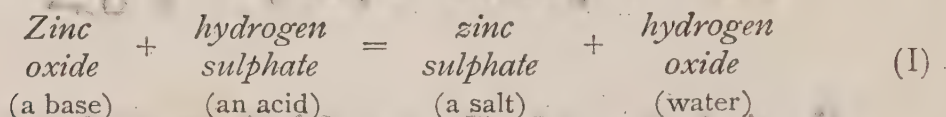
(iv) Write a verbal equation for the action in *A*.

- (v) What is formed when the new substance reacts with nitric acid?
- (vi) Write a verbal equation for the action of (v).

The insoluble hydroxides of metals can be made by double decomposition of a soluble salt of the metal and a soluble hydroxide such as that of sodium or potassium. Several cannot be obtained pure and dry.

Bases. The term *base* is primarily used to denote a substance *which reacts with an acid to form a salt and water without any other products.*

From the experiments on basic oxides (pp. 190-2) and on hydroxides (p. 193) it is plain that both these classes come under the heading of bases. The following instances are typical:—



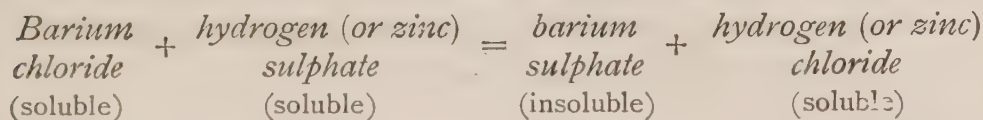
Zinc hydroxide only differs from zinc oxide in containing the elements of water in addition to the metallic oxide. Hence, if the same weight of acid is used in I and II, more water is produced in II than in I.

Methods of making salts. The same salt can usually be made in more than one way. Thus zinc sulphate has been made by the action of sulphuric acid on (a) zinc, (b) zinc oxide. It can also be made by using (c) zinc hydroxide.

Zinc sulphate is soluble in water, and is obtained from its solution by evaporating part of the water; on allowing the solution to cool, crystals of zinc sulphate separate.

Salts which are insoluble in water are made by mixing a solution of some other salt containing the required metal with another containing the required acid radical. Thus the in-

soluble salt barium sulphate was formed by the action of soluble barium chloride on a solution of hydrogen sulphate, zinc sulphate—or on almost *any* soluble sulphate.



This method is called *precipitation*—the required salt is thrown down or precipitated as a solid in the action which occurs between the two solutions.

To sum up the methods so far met with: a **soluble salt** is made by the action of an acid on

- (a) the metal (*but some metals do not react with some acids*),
- (b) the basic metallic oxide,
- (c) the metallic hydroxide.

An **insoluble salt** is made by precipitation from two solutions, one containing the required metal, the other containing the required acid radical.

Nomenclature of salts. The names given to salts are derived from the name of the acid, coupled with the name of the metal they contain. Thus:—

All salts of hydrochloric acid are called chlorides, e. g. sodium chloride.

„ „ „ nitric	„ „ „ nitrates	„ lead nitrate.
„ „ „ sulphuric	„ „ „ sulphates	„ „ sulphate.
„ „ „ sulphurous	„ „ „ sulphites	„ copper sulphite.
„ „ „ carbonic	„ „ „ carbonates	„ calcium carbonate.
„ „ „ phosphoric	„ „ „ phosphates	„ sodium phosphate.
„ „ „ oxalic	„ „ „ oxalates	„ potassium oxalate.

Exp. 5. To make soluble salts from an acid and (a) a soluble base, (b) an insoluble base or metal.

Required:—Copper oxide, sulphuric acid, two basins (medium size), stirring rod, funnel, tripod, gauze, test-tube, retort-stand and ring, porous plate.

DIRECTIONS. *A. Given a soluble* base.* Proceed as in Exp. 2, p. 189. Use litmus-paper to indicate when neutrality is reached. Evaporate to crystallizing point. This method is suitable for the chlorides, nitrates, and sulphates of sodium, potassium, ammonium; they are all neutral to litmus and soluble.

B. Given an insoluble base or metal.* These salts are usually not neutral to litmus, so that indicator cannot be used. The general method is to take a definite amount of diluted acid (1:5) and add the base or metal till no more dissolves and excess is left. Filter the solution from excess of solid and evaporate to crystallizing point, or to dryness if the salt is non-crystalline.

The majority of salts can be made in this way; each salt offers some slight peculiarity, and plenty of practice is required. The following case is typical.

To make copper sulphate crystals. Put 50 c.c. of dilute sulphuric acid (1:5) in a basin resting on gauze over a tripod.

Add *small* quantities of copper oxide, heat and stir until no more of the black solid dissolves, distinct excess being present.

Fit a funnel with filter-paper, place it in a stand and warm it by pouring hot water through. Filter the solution into a clean evaporating-basin.

(If any blue crystals remain in the funnel, stop the exit with your finger, add boiling water till they dissolve, and then let the solution run through.)

Evaporate the filtrate to the crystallizing point, i. e. until

* The terms 'soluble' and 'insoluble' refer to water, unless some other liquid is definitely mentioned.

a little of the liquid withdrawn on the end of a glass rod solidifies at once. Dry the crystals on a porous plate.

Heat a portion in an ignition tube and **observe** the effect.

Find whether it is acid, alkaline, or neutral in solution.

Label a portion in a tube, stating the method of formation.

LABORATORY RECORD. Observations on the method, effect of heat, action on litmus.

Questions:—(i) Do you recognize the blue crystals? How would you identify them exactly?

(ii) What conclusion can be drawn as to their composition?

(iii) Is the white substance left after heating the crystals a salt? Give reasons for your answer.

(iv) How can you prove that the white substance contains copper?

PROBLEMS (XII. 5).

Obtain a dry specimen of the solid product of the interaction of the following materials by the method of Exp. 5. Obtain them in crystalline form, if possible; find the effect of their solution on litmus and ascertain whether they contain water of crystallization. Name them and notice any obvious properties.

1. *Lead oxide and nitric acid.*
2. *Lime and hydrochloric acid.*
3. *Magnesium oxide and sulphuric acid.*

Exp. 6. To make insoluble salts by precipitation.

Required:—Solutions of lead nitrate and sodium sulphate, beakers, filter, &c.

PROCEDURE. *Mixing.* The general method consists in taking a definite quantity of a solution of a soluble salt of the metal—e.g. a quarter of a beakerful; to this a solution containing the required acid radical is added gradually. The mixture is stirred and the precipitate allowed to settle. More of the second solution (*precipitant*) is added until no further precipitate appears in the clear liquid.

Washing. The solid (if it settles quickly) is then washed by decantation with hot water three or four times in order to free it from the new soluble salt, simultaneously formed, and from any excess of either of the original solutions used. On

each addition of water the solid must be well stirred up and then allowed to settle. Finally, the solid is rinsed out on to a filter and the washing completed. To find when the process is finished, test a drop of the filtrate taken from the stem of the funnel for the soluble substance, e.g. if the latter is a sodium or potassium salt try the flame coloration. In some cases washing is a lengthy process. If no test can be devised, evaporate a little of the *last* portion of the filtrate; if the washing is complete there should be no solid residue.

Drying. The washed solid is dried at some temperature below its decomposition point. An air-oven at 110°C . is suitable in most cases; a steam-oven prevents the temperature rising above 100°C . Where even slight heating would decompose the salt, a desiccator (p. 56) should be used. In cases of doubt a *little* of the substance should be tried as a test.

Make a specimen of lead sulphate, using solutions of lead nitrate and sodium sulphate.

N.B.—All the common salts of sodium and potassium are soluble and are usually employed to supply the required acid radical.

LABORATORY RECORD. Description of the preparation of lead sulphate.

Questions:—(i) How did you discover when enough of the precipitant had been added?

(ii) Why is great excess of the precipitant undesirable?

(iii) What soluble salt was formed simultaneously with the lead sulphate? Write a verbal equation.

(iv) How did you discover that the washing was complete?

(v) Why are sodium and potassium salts largely used in the preparation of insoluble salts?

PROBLEMS (XII. 6). Obtain pure dry specimens of the following insoluble salts. Submit the names of the materials you propose to use for approval before starting.

1. Calcium carbonate (precipitated chalk).
2. Barium chromate.
3. Lead chloride (insoluble in *cold* but soluble in *hot* water).

Rapid filtration. In washing precipitates on a filter, time can be saved by reducing the air pressure underneath the filter-paper. The liquid then penetrates through the paper at a faster rate. Fig. 50 shows one arrangement for effecting this object. To prevent the paper from breaking, it is laid flat on a perforated disk.

The paper should fit well and be moistened before filtering is begun, any air bubbles being removed by gentle pressure.

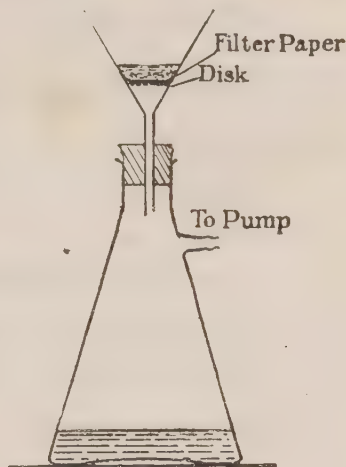


FIG. 50.

Action of solutions of salts on litmus. It must be remembered that several salts are not neutral to litmus but turn it either red or blue. The following classification of the salts already met with should be kept in mind:—

Neutral. The chlorides, nitrates, sulphates, and oxalates of potassium and sodium, i. e. salts formed from strong bases and strong acids.

Alkaline. The carbonates and sulphites of potassium and sodium, i. e. salts formed from strong bases and weak acids.

Acidic. Copper sulphate, zinc sulphate, zinc chloride, &c., i. e. the salts of weak bases and strong acids.

Peroxides of metals. These contain a greater percentage of oxygen than the basic oxide of the same metal. Manganese dioxide (p. 104) and barium dioxide (p. 109) are examples. They are distinguished from basic oxides as follows:—

(a) On heating, oxygen is evolved and a lower oxide (often the basic oxide) remains.

(b) On warming with sulphuric acid, water and the metallic sulphate are formed together with oxygen gas.

(c) On warming with hydrochloric acid, water, the metallic chloride, and chlorine gas are formed. This action is investigated in the next experiment.

Exp. 7. To examine the action of peroxides on hydrochloric acid.

Required:—Manganese dioxide, litmus-paper, test-tubes, basins.

DIRECTIONS. *A.* Fill a quarter of a test-tube with a strong solution of commercial hydrochloric acid. Add a few small pieces of manganese dioxide (= peroxide), warm *gently* and **note** what happens. Put a piece of moistened litmus-paper in the mouth of the tube and **note** the colour change, which is used as a test for the gas.

B. Allow the action to continue in a draught-chamber till no more of the green gas (called *chlorine*) is given off. Filter and evaporate the filtrate in a draught-chamber to crystallizing point.

LABORATORY RECORD. Observations in *A* and *B*.

Questions:—(i) What elements does manganese dioxide contain?
 (ii) Where must the chlorine have come from?
 (iii) To what class of compound do you expect the crystals obtained in *B* to belong?
 (iv) What gas is obtained by heating manganese peroxide (dioxide)?
 (v) What two substances have you proved to be obtainable from hydrochloric acid?

PROBLEM (XII. 7). Investigate the action of hydrochloric acid on *red lead* and determine whether it is a peroxide or not.

Classification of oxides. From the experiments of this and preceding chapters it will be seen that oxides may be conveniently divided into four groups.

(1) *Acidic oxides*, e.g. carbon dioxide, sulphur dioxide, sulphuric anhydride, phosphoric oxide, &c.

(Nearly all are oxides of non-metals, but some are the higher oxides of metals, e.g. chromium trioxide.)

(2) *Basic oxides*, e.g. oxides of magnesium, copper, mercury, tin, lead (litharge), zinc, iron, together with the sub-group

of *alkaline oxides*, viz. the lower oxides of sodium, potassium, and calcium. (These are all metallic oxides.)

(3) *Peroxides*, a small group, e. g. manganese dioxide, red lead, barium dioxide, &c. They contain a higher percentage weight of oxygen than the basic oxide of the same metal.

(4) *Indifferent oxides*, e. g. water.

Other members of each group will be met with later.

QUESTIONS ON CHAPTER XII.

1. Describe the action of concentrated sulphuric acid on salt, and explain how both products can be collected. How is the solid product identified?

2. Describe experiments to illustrate the properties of hydrochloric acid. What is the test for it? How would you distinguish between a solution of the acid and a solution of common salt?

3. How would you make crystals of common salt, given hydrochloric acid, and any other materials?

4. Give an account of an experiment to show that when a dry acid acts on a dry basic oxide, water is one of the products.

5. Define a basic oxide. Name three, and state what would be formed by their action with hydrochloric and sulphuric acids.

6. How can an insoluble metallic hydroxide be made? What happens when it is heated, and how can you prove your answer to be correct?

7. What is a base? Give four examples and write verbal equations for their action with sulphuric acid.

8. Describe *in detail* how copper sulphate crystals can be made from copper oxide and sulphuric acid. Has the salt a neutral or an acid reaction? How is white copper sulphate made?

9. Explain the procedure of making an insoluble salt like barium sulphate, given a solution of barium chloride.

10. What are the chief characteristics of peroxides? State the action of manganese peroxide on hydrochloric acid, and describe the properties of the gas produced.

11. Define the term salt. Enumerate several ways in which a given salt can be made, writing verbal equations for the actions.

CHAPTER XIII

HYDROGEN AND WATER

Preliminary Questions. 1. By what three methods have you obtained hydrogen from water?

2. What substance do you expect to be formed when hydrogen burns in air?

3. By what reaction was hydrogen obtained from diluted sulphuric acid?

4. How do you know that the hydrogen (of question 3) really came from the acid and not from the water used to dilute it?

5. What other product was obtained in the action of question 3?

6. On what grounds do you conclude that hydrochloric acid contains hydrogen?

Exp. 1. To prepare hydrogen (usual laboratory method).

Required:—As in Fig. 51; granulated zinc, diluted sulphuric acid (1 : 5), test-tubes.

DIRECTIONS. *A.* Set up the apparatus shown in Fig. 51.

Test it for leaks by closing the end of the delivery-tube with your finger, and pouring water into the funnel. If water enters the flask, there is a leak

in the cork, or rubber connexion, which must be made good.

Carefully *slide* in enough granulated zinc to cover the bottom of the flask. Fix the cork, and add acid through the funnel until the zinc is covered.

Note what happens.

Precaution :—*No flame must be brought near.*

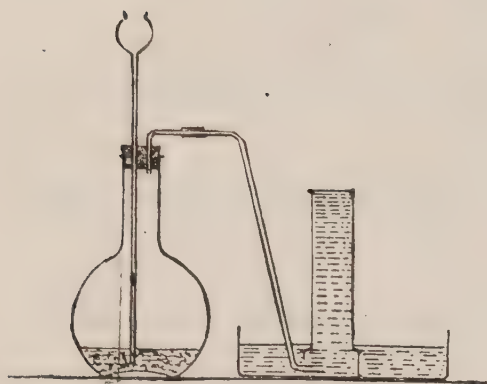


FIG. 51.

Fill a *test-tube* with water and invert it over the end of the delivery-tube. When full of gas, *close the mouth of the test-tube* with the thumb, remove it from the trough and hold it, mouth downwards, over a flame placed some distance away. **Note** the effect, and repeat until this is no longer observed.

Collect more of the gas in test-tubes and in gas-jars while doing *B.* **Note** its obvious properties—*colour, smell, solubility in water (if any), &c.*

B. Find the cause of the explosion. Fill three-quarters of a tube with water; invert over the delivery-tube so as to fill it up with hydrogen. Close with the thumb and bring it over a flame as before.

Repeat, using equal volumes of hydrogen and air, and also five times as much air as hydrogen. **Note** which proportion gives the loudest report.

- C. Find whether hydrogen is lighter or heavier than air, by ascertaining whether it can be transferred to a tube containing air, by pouring it upwards or downwards; test by putting the second tube over a flame.
- D. Find whether hydrogen supports the combustion of a taper, by pushing a lighted taper into the middle of a jar of the gas. **Note** whether it is extinguished or not.
- E. Fill a jar with hydrogen, cover the mouth with a plate, and place it mouth downwards over a jar of air. Remove the plate carefully and let the jars remain for 3 min. Slip in two cover-plates between the jars, remove the upper jar, and turn it right side up. Bring a lighted taper to the mouth of each jar. **Note** the result.

[N.B.—Keep the contents of the flask for Problem below, and keep the generator for Exp. 2 onwards.]

LABORATORY RECORD. Diagram of actual apparatus used. Observations, *list of observed properties* of hydrogen.

Questions:—(i) Give a reason for the precaution in A.

- (ii) How can hydrogen be distinguished from all the other gases you have made?
- (iii) Does hydrogen support the combustion of a taper?
- (iv) In what two ways may the gas be collected? Which do you consider best, and why?
- (v) Considering that there is water in the flask, would you expect the hydrogen to be dry?
- (vi) What has become of the zinc?
- (vii) In E, was (a) hydrogen, (b) air found in both jars?
- (viii) Try to explain result of E.
- (ix) Examine Kipp's apparatus for making hydrogen. Draw a diagram and explain how it works.

PROBLEMS (XIII. 1). 1. When no more zinc dissolves in the flask used in Exp. 1 (if all has dissolved add more zinc), filter from excess of zinc and evaporate in a basin to crystallizing point. State what the crystals are and find whether they contain zinc.

2. Examine the action of magnesium, iron filings, lead, and copper on (a) concentrated, (b) diluted sulphuric acid. Use test-tubes.

The diffusion of gases. Although hydrogen is much lighter than air, Exp. 1, *E*, shows that it descends into a jar of air, and that the heavy air rises and mixes with the hydrogen. Such intermixture, against the action of gravity, is called diffusion. Air affords another instance; oxygen is slightly heavier than nitrogen, yet the relative proportions of the two is the same at sea-level as on a mountain. Again, if

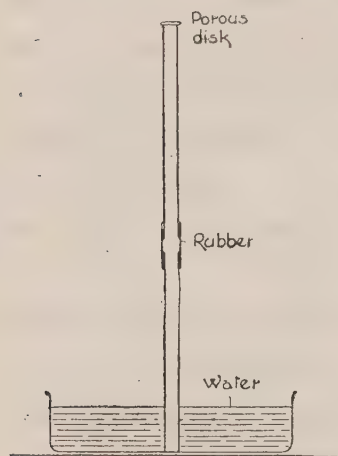


FIG. 52.

coal-gas escapes into a room, it can be smelt at all parts of the room and does not wholly rise to the top as might be expected. Diffusion has therefore to be recognized as a common property of gases, and may be defined as *the process by which gases mix with one another instead of forming distinct layers according to their density.*

The facts of diffusion were investigated by Graham in 1832. He used glass tubes closed at one end by porous materials such as plaster of Paris, graphite, &c. Such an instrument is called a *diffusiometer*. Fig. 52 shows a simple form suitable for the next experiment. It consists of two pieces of glass tube (1 cm. wide and 20 cm. long) joined by a piece of sound rubber tubing. The top is closed by a thin disk of unglazed earthenware cemented on, or by a plug made by dipping the end of the tube into a paste of plaster of Paris.

Exp. 2. To study the diffusion of hydrogen, coal-gas, and air.

Required :—Kipp or other hydrogen generator, diffusionmeter as in Fig. 52, basin, rubber bands.

DIRECTIONS. *A.* Attach a narrow glass tube to a hydrogen generator, push it into the diffusion tube, and pass hydrogen in for some minutes. Cover the disk with a piece of paper, place your thumb over it and withdraw the delivery-tube slowly. Close the other end of the tube with a finger and transfer it to a shallow basin of water (Fig. 52) and clamp it. *Avoid wetting the porous disk.*

Observe it for some time and mark the highest point to which the water rises with a rubber band.

Close the top with paper and thumb as before, detach the upper tube, closing with a finger, but leaving the rubber on the lower one. Test the contents for hydrogen.

B. Refix the diffusion tube and lower rubber band to about one-third of its previous height.

Refill with hydrogen as before, and **note** the time the water takes to rise to the mark.

C. Shake out the water and refix the diffusion tube with its open end dipping into water. Invert a beaker over the top of the tube and fill the beaker with hydrogen by upward displacement. **Note** what happens.

D. Repeat *B* and *C*, using coal-gas, leaving the band in the same position and keeping all other conditions exactly the same. **Note** the time taken by the water in rising.

LABORATORY RECORD. Diagram ; give the times for both gases.

Effects observed with (a) air inside, hydrogen outside.

(b) coal-gas „ air „

(c) air „ coal-gas „

Questions :—(i) In *A*, why did not the water rise to the top of the tube?

(ii) Was the gas in the top part of the tube, hydrogen, air, or a mixture, when tested?

(iii) Explain the result of *B*.

(iv) Arrange the three gases in the order of their densities.

(v) Which diffuses quickest and which slowest?

Graham's law of diffusion. Exp. 2, p. 207, will have shown that when a porous partition is placed between two gases of different densities, both penetrate through it, but at different rates. The lighter gas penetrates, or diffuses, more rapidly than the heavy one.

Graham, who investigated the phenomenon, found that 3.83 volumes of hydrogen, 0.812 vol. of carbon dioxide, and 1 vol. of air diffused through a partition in the same time. Hence the rate of diffusion of hydrogen is 3.83 times the rate of diffusion of air, and $\frac{3.83}{0.812} = 4.7$ times the rate of diffusion of carbon dioxide. He then noticed that these numbers were related to the densities of the gases in the following way. Taking the density of hydrogen as 1, then the density of air is 14.4, and of carbon dioxide 22, we find that the square root of $14.4 = 3.8$ and of $22 = 4.7$. Hence he was able to sum up all the facts he discovered about the diffusibility of gases in the following statement or law:—

The rates of diffusion of any two gases are inversely proportional to the square roots of their densities.

For example :

$$\frac{\text{Rate of diffusion of hydrogen}}{\text{Rate of diffusion of air}} = \frac{3.83}{1} = 3.83 \text{ (by experiment).}$$

$$\frac{\frac{1}{\sqrt{\text{density of hydrogen}}}}{\frac{1}{\sqrt{\text{density of air}}}} = \frac{\frac{1}{\sqrt{1}}}}{\frac{1}{\sqrt{14.4}}}} = \frac{\sqrt{14.4}}{\sqrt{1}} = \sqrt{14.4} = 3.8.$$

Purification of hydrogen from acid spray, moisture, and air. When the gas is made by the action of a metal on an acid, as each bubble of gas bursts the film of liquid acid breaks up into minute drops, which are carried over with the gas. This is prevented by passing the gas through a U-tube (or a straight tube about 6 in. long) packed with cotton-wool.

Any gas prepared in the presence of water will contain water *vapour*, which is not kept back by the wool. To remove this, pass the gas through a second U-tube, *carefully* packed with calcium chloride. The packing must be arranged so as to make the gas thread its way through narrow passages between the bits of solid so that the *whole* of the gas comes in contact with the drying agent.

When making hydrogen it is most important to avoid leaks in corks, &c., and to be careful not to inflame the gas before all the air has been driven out of the apparatus.

Precaution :—*Before collecting hydrogen for experiments, and especially before lighting it at a jet, fill a test-tube with the gas, and test it with a flame. This must be repeated until a tubeful is obtained which burns quietly and without explosion. It is then free from air.*

Exp. 3. To examine the products formed by burning hydrogen in (a) air, (b) chlorine.

Required:—Hydrogen generator, U-tubes, cotton-wool, calcium chloride; boiling-point apparatus, jar of chlorine, and as in Figs. 53 and 54.

DIRECTIONS. *A.* Connect the hydrogen generator first with

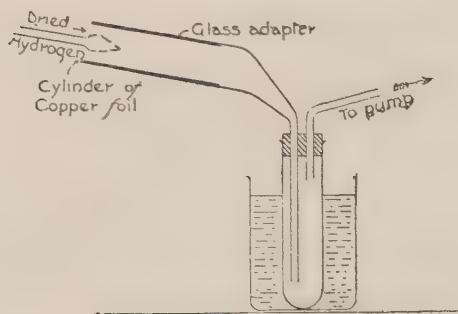


FIG. 53.

a U-tube containing cotton-wool, next with a U-tube packed (see p. 209) with calcium chloride, and this with a glass jet, as in Fig. 53.

Collect a tubeful of the gas and test it as usual, until free from air. Then

light the hydrogen, start the pump and place the jet in the mouth of the wide tube.*

Collect about 2 c.c. of liquid and determine its density and then its boiling-point.

Read the barometer and find the temperature of the air.

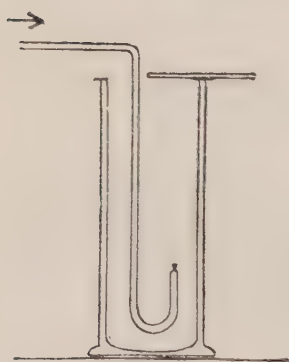


FIG. 54.

B. Put a jar of chlorine in a draught-chamber and place a jet of burning hydrogen in it as shown in Fig. 54.

Note what happens.

Withdraw the jet, add a little water, cover the jar and shake. Identify the substance dissolved by the water, using any suitable tests.

LABORATORY RECORD. Diagram, explanations, and observations. Record of the density and B.P. of the liquid in *A*.

Questions:—(i) What liquid boils at the temperature and pressure noted in *A*?

(ii) What liquid has the density observed, at the temperature of the room?

(iii) What substance is produced in *B*?

* A glass adapter with a cylinder of copper-foil put inside to prevent the glass from cracking.

Exp. 4. To show the reducing action of hydrogen.

Required:—Hydrogen generator, hard-glass tube, &c., as in Fig. 55.

DIRECTIONS. Set up the apparatus shown in Fig. 55 and attach the hydrogen generator to the U-tube. At first arrange the right-angled delivery-tube with its mouth pointing upward (not as in Fig. 55).

Precaution :—*Read precaution on p. 209.*

Make hydrogen and collect it in test-tubes until it is proved to be pure, by the *absence* of an explosion on ignition.

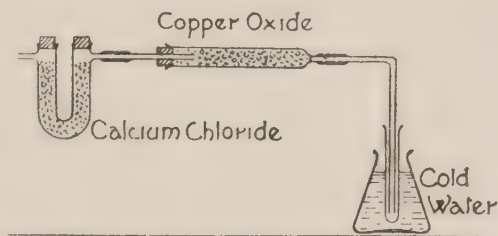


FIG. 55.

Note whether the copper oxide appears to change or not.

Turn the end of the delivery-tube downwards so as to pass into a dry test-tube cooled by water, and *gently* heat the copper oxide, being careful to avoid burning the corks. Continue to heat until the whole of the oxide is changed. Remove the flame and allow hydrogen to pass through the tube until it is cold.

Try to identify both the solid in the hard-glass tube and the liquid in the test-tube.

LABORATORY RECORD. Diagram, observations, and difficulties.

Questions :—(i) What impurity was removed from the hydrogen before it was used in this experiment?

(ii) What substances were formed by the action of hydrogen with copper oxide? By what properties were they recognized?

(iii) Which substance is the reduction product and which the oxidation product?

(iv) Does any apparent action take place in the cold?

PROBLEMS (XIII. 4). I. Repeat Exp. 4 with *iron oxide* which has been carefully dried, by previous heating for 15 minutes on a sand-tray.

[Over.

If the oxide loses oxygen the substance left ought to be magnetic. Compare it with the unchanged oxide in this respect.

2. Try a similar experiment with *lead oxide*, using *coal-gas* as the reducing agent. Consider the characteristic properties of lead and find whether this metal is formed.

Exp. 5. To detect the presence of hydrogen in compounds.

Required:—Dry copper oxide, naphthalene or spermaceti, ignition tube, mortar.

DIRECTIONS. Quickly mix a *little* of the substance to be tested (naphthalene or spermaceti) with ten times its bulk of *recently dried* copper oxide in a mortar. Half fill an ignition tube with the mixture and wipe out any solid from the upper part of the tube. Hold it horizontally in a flame and **note** whether any liquid forms in the cool part of the tube. If it does, test it with white copper sulphate.

This method is suitable for liquids as well as solids; *small* quantities should be used, and the copper oxide being hygroscopic must have been well dried beforehand. Hydrogen may be detected in gases as in Exp. 4.

LABORATORY RECORD. Description and observations.

Questions:—(i) If a substance when heated *alone* in a tube yields water, what conclusion can be drawn respecting the composition of the substance?

(ii) What change did the copper oxide undergo?

***Exp. 6.** To determine the gravimetric composition of water.

Required:—As in Fig. 56; silver sulphate solution, sulphuric acid (concentrated), pumice, hard-glass tube 12 cm. long, freshly dried copper oxide (granular), hydrogen generator, water-pump.

The object of the experiment is to pass purified hydrogen over a known weight of hot copper oxide, to collect and weigh the water formed, and to find the weight of oxygen lost by the copper oxide.

The details of the apparatus are shown in Fig. 56. A contains a solution of silver sulphate to absorb arsenic hydride.

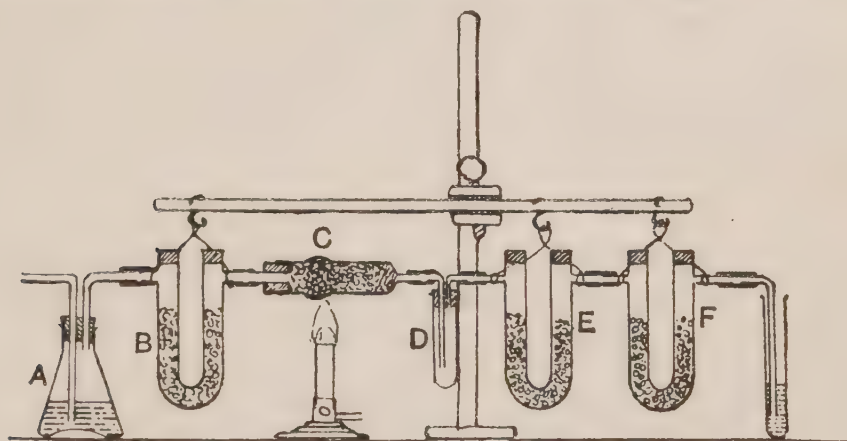


FIG. 56.

This is liable to be mixed with the hydrogen when common zinc (containing arsenic) is used.

B contains pumice moistened with sulphuric acid for drying the hydrogen to remove water vapour.

C is a hard-glass bulb-tube containing granulated copper oxide, previously ignited for the purpose of drying it.

D is a short test-tube in which most of the water collects.

E and F are U-tubes containing sulphuric acid on pumice; in these is collected all the water which is not condensed in D.

G is a test-tube containing a little water, to show the rate at which the hydrogen is passing through the apparatus.

[Over.

* Demonstration.

Weighings:—(i) c with its cork and connecting tube.

(ii) D, E, and F are weighed together, glass plugs being first pushed into the rubber connexion at each end.

Procedure. The parts of the apparatus are connected and a stream of hydrogen is passed through, the rate being regulated so that about four bubbles pass out at G per second. (If no bubbles appear at G, there is a leak which must be discovered and stopped.)

After a few minutes, a test-tubeful of the gas issuing from G is collected and tested in the usual manner.

c is now gently heated from end to end, so as to avoid cracking; then the temperature is gradually raised until reduction of the copper oxide begins. The heating is continued for some minutes after complete reduction has taken place and all signs of water have disappeared from c.

The flame is now removed, but hydrogen is still passed through, until c is quite cold.

A slow stream of air is drawn through the apparatus by means of an aspirator at G, so as to displace the hydrogen.

Final Weighings:—(iii) c, (iv) D, E, and F; with the same connexions and glass plugs as before.

LABORATORY RECORD. The results are entered thus:—

Weight of c with copper oxide (*before heating*) = — g.

„ „ „ copper (*after heating*) . . = — g.

Weight of oxygen lost by the copper oxide . . = — g. (*x*)

Weight of absorption tubes D, E, F *after exp.* = — g.

„ „ „ „ *before exp.* = — g.

Weight of water formed = — g. (*y*)

∴ *y* grams of water contain *x* grams of oxygen and *y* − *x* grams of hydrogen.

Questions:—(i) Calculate the percentage weights of hydrogen and oxygen in water.

(ii) Why is a *slow* current of hydrogen better than a rapid one?

(iii) Why is air drawn through before the last weighings?

(iv) Why must c be *cool*, before air is passed through it?

(v) What weight of oxygen combines with 1 g. of hydrogen?

Sources of error in Experiment 6. It is probable that the result obtained is not correct, since the accurate determination of the composition of water is a matter of extreme difficulty. The reasons for this are as follows:—

(a) It is very difficult to obtain hydrogen free from traces of water, air, hydrides of arsenic, and other impurities present in the zinc and acid.

(b) Metallic copper has the power of absorbing small quantities of hydrogen, which makes the loss in weight of the copper oxide (i. e. the weight of oxygen) too low.

(c) The hydrogen is obtained as a very small difference in weight between two much larger ones; for example, the actual weight of the water absorption tubes may be 70 g., but the weight of hydrogen in the water formed in the experiment may not be more than 0.05 g., and a very small error in weighing makes a large percentage error on the hydrogen.

Exp. 7. Further examination of the action between sulphuric acid and zinc.

Required:—Insoluble residue from hydrogen generator or Kipp, scrap porcelain, pure and commercial zinc, copper wire, test-tubes.*

DIRECTIONS. *A.* Shake up the residual liquid in a hydrogen generator which has been in use for some time and filter it to collect the small black specks, but not the bigger pieces of zinc. Wash the specks with water.

Scrape off some of the black solid and **note** whether it dissolves in dilute sulphuric acid or not. **Note** also the result of heating it on a bit of porcelain in a Bunsen flame so as to oxidize it. Try to identify the oxide by its colour. [Over.

* Kahlbaum's pure granulated zinc (obtainable from J. J. Griffin & Son, Kingsway, W.C.) is suitable.

B. Put a piece of (*a*) pure, (*b*) commercial granulated zinc in separate test-tubes and cover them with pure dilute sulphuric acid. **Note** any effect and observe both at intervals for 10 min.

C. Repeat *B*, using *concentrated* sulphuric acid and dry tubes. **Note** results.

D. Repeat *B*, but place a piece of copper wire in each tube. **Observe** the effect when the metals (*a*) are, and (*b*) are not in contact. If bubbles of gas are set free, **note** from which metal they seem to come.

LABORATORY RECORD. Full observations.

Questions:—(i) In *A*, are the black specks zinc? If so, give evidence of it; if not, what metal or metals do you think they contain?
(ii) Does pure zinc react with (*a*) dilute, (*b*) conc. sulphuric acid?
(iii) Does commercial zinc react with conc. sulphuric acid?
(iv) From observations made in *D*, suggest a reason for the action of commercial zinc with *dilute* sulphuric acid.

Exp. 8. To observe the joint action of pure zinc and copper on sulphuric acid.

Required:—Plates of amalgamated zinc and of copper as in Fig. 57, small galvanometer, connecting screws and insulated wire, chromic acid.

DIRECTIONS. Half fill a glass jar or beaker with dilute sulphuric acid (1:20), and put a plate of amalgamated zinc in it.

[If the zinc is not already amalgamated, rub it with a rag dipped in hydrochloric acid, put a *small* drop of mercury on the plate and rub the mercury over both sides with the rag. The mercury forms a layer over the zinc, due to a compound or amalgam of zinc and mercury. Such a plate acts like a plate of *pure* zinc.]

Then put in a plate of copper (this must *not* be covered with mercury) and attach insulated copper wires to each. Fig. 57 shows a convenient form of the apparatus. The wires are to be attached to the binding screws. Join the

wires and **note** what happens in the vessel. Put the end of one wire underneath and the other on the top of the tongue and **note** the effect. Attach the wires to the terminals of a small galvanometer (i. e. a compass needle with a coil of insulated copper wire round it; see Fig. 58).

Place the galvanometer so that the needle is parallel to the coil. **Note** the effect on the needle.

Interchange the wires connected with the galvanometer and again **note** the effect on the needle. Leave for 5 min. and **note** any effect on the needle.

Without stopping the current, add a little red oxide of chromium or a few drops of chromic acid. **Note** any change on the surface of the copper, the effect on the needle, and on the colour of the solution after 10 min.

This arrangement forms a *voltaic couple or electric cell*. When there is contact between the plates by means of a wire or other conductor, an electric current is generated and the chemical action between the zinc and the acid takes place. When contact is broken, both the current and the chemical action stop. A galvanometer is used to detect and to measure the intensity of an electric current. The coil should be in the vertical plane of the needle when no current is passing.

LABORATORY RECORD. Diagram and observations.

Questions :—(i) Did the amalgamated zinc react with the acid when unconnected with the copper?

(ii) Does copper alone react with dilute sulphuric acid?

(iii) How can the presence of an electric current in a wire be detected?

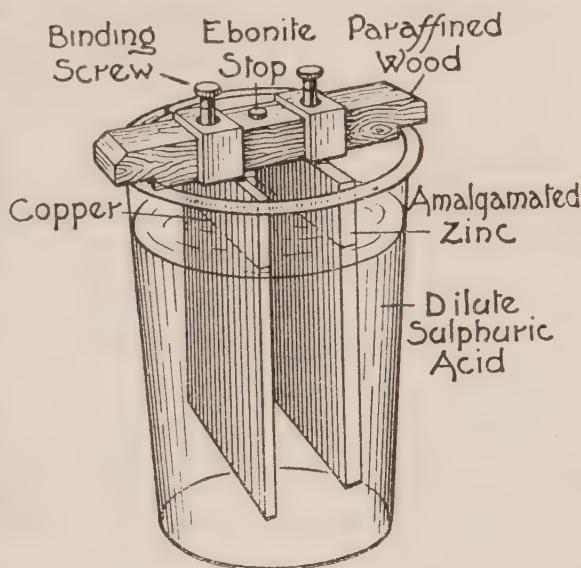


FIG. 57.

**The conditions under which sulphuric acid acts
with zinc.**

Exp. 7 (C) (p. 216) shows that the concentrated acid has only a momentary action on common zinc, hence the *presence of water* is a necessary condition for continuous action.

Exp. 7 (B) shows that even diluted acid has scarcely any action if the zinc be pure, but that the presence of a *small quantity of another metal* (as in common zinc) is necessary.

This caused us to investigate the joint action of pure zinc and copper on the diluted acid (Exp. 8), resulting in the discovery of the facts (a) that hydrogen is only produced when the metals are in contact, or when joined by a copper wire; (b) that the gas seems to come from the surface of the copper, and little, or none, from the zinc; (c) that a peculiar sensation is produced on the tongue when in contact with both metals.

This sensation is due to a current of electricity, so that the action of zinc on the acid is associated with the generation of an electric current. The current is immediately produced when impure zinc is put into acid, but pure zinc requires to be in contact with a second metal before a current can be formed and the chemical action can begin.

If both plates used in Exp. 8 are weighed beforehand, and again after the action has proceeded for some time, it is found that the weight of the copper remains unchanged, but that of the zinc decreases. Hence the copper plays no part in the chemical change. When all the acid is used up, the jar contains a solution of zinc sulphate.

If the action of sheet zinc is compared with that on granulated zinc, it is found that the former soon becomes covered with bubbles of hydrogen which keep the acid from contact with the metal. But when the zinc is granulated and covered with many sharp points, the bubbles get away more

quickly, and so the action is more continuous. Hence a *rough surface* is better than a smooth one.

The conditions for a continual and rapid evolution of hydrogen from a mixture of sulphuric acid and zinc are—

- (1) *Diluted acid.*
- (2) The presence of a second metal, such as copper.
- (3) *Granulated zinc.*

Voltaic cells. Besides the simple cell used in Exp. 8 a large number of others have been devised. They consist of two plates—one (usually of zinc), which dissolves in the liquid, is known as the *negative plate*; the second, which is unaffected by the liquid, is called the *positive plate*. When these plates are joined by a wire, a current flows through the wire from the positive to the negative plate.

Local action. If the zinc plate in Exp. 8 had not been amalgamated, hydrogen bubbles would have appeared on it as well as on the copper. This is due to little local currents between the foreign metals in the commercial zinc and the zinc itself. Such local action reduces the strength of the current, and is prevented by a coating of mercury. The mercury dissolves the zinc in preference to the other metals, thus presenting pure zinc to the acid, which dissolves it when the plates are joined. Fresh zinc is dissolved by the mercury, and so on. The solution or alloy of zinc and mercury is called an amalgam.

Polarization. Exp. 8 will have shown that the strength of a current diminishes after a short time, and that a large part of the copper or *positive* plate is covered with hydrogen bubbles. When this occurs the plate is said to be polarized.

The addition of red oxide of chromium or its solution (chromic acid) prevents the formation of these bubbles by oxidizing them with formation of water. Simultaneously the chromic acid is reduced to the lower oxide (the green oxide), which is basic.

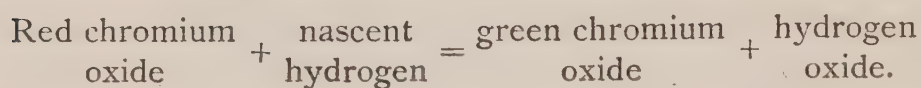
Any liquid used for prevention of an accumulation of

hydrogen on the positive plate is called a depolarizing fluid. It is found best to keep this from mixing with the exciting fluid (e.g. sulphuric acid) by putting the positive plate in a porous vessel surrounded by the depolarizer. Since chromic acid dissolves copper, a plate of gas carbon is used instead; care must always be taken that the depolarizer has no chemical action on the positive plate. Nitric acid and manganese dioxide are also used as depolarizing substances.

An *electric battery* is formed by joining several cells so that the negative plate of one is connected with the positive of the next in the row. On connecting the extreme plates (called the poles of the battery) by a wire, a stronger current flows through it than is obtainable from a single cell.

Nascent hydrogen. If a stream of ordinary hydrogen is passed through a solution of chromic acid, the reduction to the green oxide (Exp. 8) is not observed. Similarly, ordinary hydrogen does not reduce copper oxide except when hot, but if a little copper oxide is placed with some zinc and sulphuric acid, immediate reduction to copper occurs.

Owing to these facts and many others of a similar kind, we have to distinguish between the chemical activity of hydrogen which has been collected in bulk and that which exists in minute particles at the moment of its liberation from a substance such as sulphuric acid. Hydrogen in the latter, and chemically more active state is called nascent hydrogen.



Voltameters. In order to pass an electric current through a liquid an instrument called a voltameter is used. It consists essentially of a vessel holding the liquid into which the wires conveying the current can be fixed. Instead of dipping the ends of thin copper wires into the liquid, it is found better to connect them to sheets of platinum. **The**

increase of surface enables the current to pass more easily, and platinum has no chemical action on the majority of liquids. These platinum plates are called *electrodes*; that connected with the positive pole of the battery is the *positive electrode* or *anode*; the other is the *negative electrode* or *kathode*. Many different forms of voltameter are used, but they only differ in detail and not in principle. A common form is shown in Fig. 58.

Exp. 9. To find the effect of an electric current on water and dilute solutions of an acid, alkali, and sugar.

Required:—As in Figs. 58 and 57; sugar, sulphuric acid, sodium hydroxide, distilled water, glass siphon.

DIRECTIONS. Set up the apparatus as in Fig. 58, turning the galvanometer till the coil is in the same vertical plane as the needle.

Connect one pole of the battery to the galvanometer and the other to the voltameter, which is to be *empty* at first.

Attach the free wire of the galvanometer to the other binding screw of the voltameter.

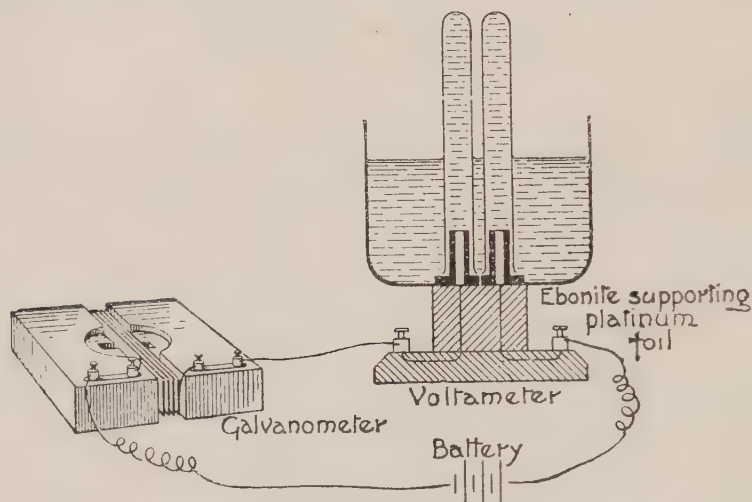


FIG. 58.

After the circuit is closed, **note** whether the needle is deflected or not.

Place the following liquids successively in the voltameter so as to cover the platinum plates (electrodes):—

(a) Pure distilled water; (b) solution of sugar in distilled water; (c) distilled water containing a few drops of sulphuric acid (test the liquid with blue litmus-paper after the current has been passing for some time); (d) dilute solution of sodium hydroxide.

Siphon off each liquid and thoroughly rinse the voltameter with water before adding the next.

Note the effects on the needle and liquid (if any) in each case.

If any gas is produced, invert test-tubes full of water over each plate of the voltameter. When one tube is nearly full, break the circuit, by releasing the wire from any binding screw; remove the tubes, carefully closing the open end with your thumb.

Test each for hydrogen and oxygen, **noting** from which plate the particular gas came.

Roughly estimate the relative volumes of the gases.

LABORATORY RECORD. Careful observations for each liquid. Diagram of *actual* apparatus used.

Questions:—(i) Which liquids conduct electricity, and which do not?

(ii) Which solutions yield gases?

(iii) Name the gases and state from which electrode they come in each case.

(iv) Is the sulphuric acid solution still acid after the current has passed for some time?

(v) How would you arrange an experiment to discover whether any of the acid has been used up when electricity is passed through acidulated water?

Electrolysis. Although pure water is a non-conductor of electricity (Exp. 9, *a*), it was found that the addition of a very small quantity of sulphuric acid (Exp. 9, *c*) enabled a current to pass through it, and caused hydrogen to be given off at the kathode (negative electrode of the voltameter) and oxygen at the anode. Large quantities of these gases can be obtained in this way with a very small amount of acid. If we had put in a known volume of sulphuric acid and had known how many c.c. of caustic soda solution this would neutralize, then on neutralizing the acid left in the voltameter after much gas had been collected, we should have found that there was as much acid at the end as there was to begin with. Hence the gases have not been generated from the acid, but from the water. The presence of an acid or alkali is a necessary condition for the passage of electricity through the water, and the effect of this is to decompose or analyse the water into its elements. When a substance like water is decomposed by electricity the process is called *electrolysis*.

Certain acids, alkalis and, as will appear later, salts, which dissolve in a non-conducting liquid like water, and cause it to become a conductor, are called **electrolytes**, while substances like sugar which have not this effect are *non-electrolytes*. An electrolyte is also called a 'conductor of the second class', to indicate that decomposition occurs when it conducts, which is not the case in 'conductors of the first class', such as metals.

Another important fact observed during the electrolysis of water was that the volume of hydrogen produced is approximately double that of the oxygen. Thus we have incidentally performed a volumetric analysis of water.

Chemical synthesis and electricity. In electrolysis the electric current causes chemical decomposition, but electricity may also be used to effect combination or synthesis. For this purpose an electric spark is employed as a convenient source of heat. A spark is obtained when a discharge of electricity passes through an air space between two parts

of a circuit. If a very powerful battery is used and the wires from the two poles are connected and then separated, a spark will pass across the gap. The batteries we have used will not produce a spark (at any rate not a long one). They may be the cause of one, however, if joined to a Ruhmkorff induction coil. The principle of this coil depends on the following fact:—If an intermittent current (i. e. one which is frequently started and stopped) is passed through a coil of wire, a powerful 'secondary' current is induced in a second coil wound over (but not in contact with) the first, whenever the original or primary current is started or stopped. If the terminals of the secondary coil are brought near together, a spark passes between them. For further details, a book on Electricity should be consulted.

The Eudiometer. In effecting the volumetric synthesis of gases, it is necessary to use a vessel in which their volumes, both before and after combination, can be measured under known conditions of temperature and pressure. The first instrument for this purpose was invented by Cavendish and used by him for finding the proportion of oxygen in air, or as he expressed it, its goodness. This was done by exploding a measured volume of air with hydrogen, and observing the contraction due to the formation of water.

A convenient form of eudiometer or gas analysis apparatus is shown in Fig. 59. It consists of a U-tube made of thick glass closed at each end by taps. At the bottom of one limb *r* is another tap *A*, to which is bound a length of thick-walled rubber tubing terminating in a glass reservoir *D*.

Through the glass at the top of the right-hand limb *G* are sealed two platinum wires, so as to leave a short gap between their ends inside the tube. An electric spark can be passed across the gap when the wires are connected with a suitable source of electricity.

The limb (*G*) carrying the wires is called the explosion tube, and is surrounded by a glass jacket *E* containing water;

the temperature of the water will be the same as that of the gas in the tube.

Both limbs of the eudiometer are graduated; the graduations of the explosion tube (G) being in tenths of a c.c., starting at the tap and going downwards, those on the other limb (F) in mm.

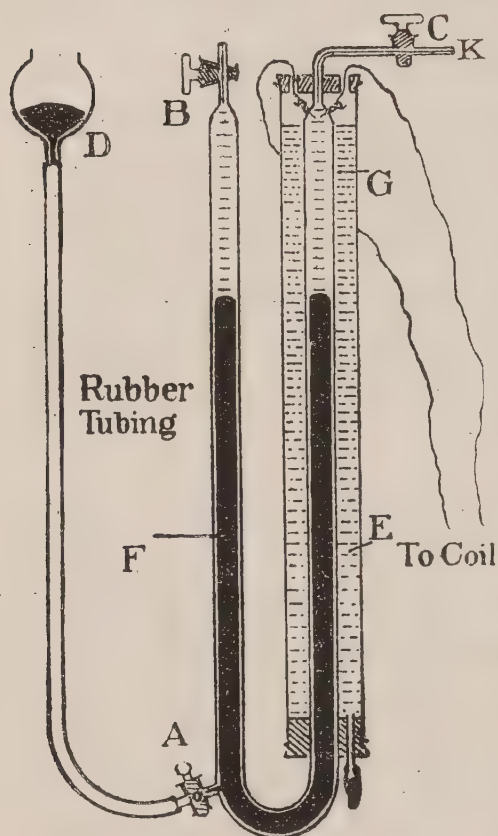


FIG. 59.

In order to compare the volumes of gases, they must either have been measured at the same pressure and temperature, or, if not, the actual conditions under which each volume was measured must be known and both reduced to the same conditions by calculation (p. 68).

The advantage of the eudiometer shown in Fig. 59 is that all volumes can be measured at the same pressure, viz. that of the atmosphere. Thus, if the tap B is open and G contains gas, the latter will be under atmospheric pressure when the

levels of the mercury in the two limbs of the U-tube are the same. If the levels are not the same, the tap A is opened and the reservoir D is raised or lowered until the mercury levels F and G are the same.

***Exp. 10. To find the proportions by volume in which hydrogen and oxygen combine to form water.**

Required:—Battery, Ruhmkorff coil, eudiometer as in Fig. 59, hard-glass test-tubes with cork and exit-tube, hydrogen generator, potassium chlorate, 18 inches of rubber connecting tube.

Enough mercury having been poured into the reservoir D to fill both limbs of the eudiometer, the tap A is opened and B is *closed*. C is now carefully turned on until the explosion tube is nearly full of mercury.

A little water is then drawn into the top of the explosion tube, so that the gas, subsequently introduced, may be saturated with water vapour. G having been filled with mercury to the end of the exit-tube, C is closed, B is opened, and D is lowered.

Introduction and measurement of the oxygen. One-third of a hard-glass test-tube is filled with potassium chlorate, and clamped at a convenient height, and after being fitted with a cork, exit-tube, and long piece of rubber tubing, it is heated until oxygen begins to come off freely. When all air has been expelled, the end of the rubber tubing is quickly attached to K (see Fig. 59) and C is opened. The mercury at once falls in the explosion tube, and when about 10 c.c. of gas have entered, C is closed and the rubber connexion is removed.

By moving the reservoir up or down the levels of the mercury in the two limbs (F and G) can be brought to the same height. When this is the case the oxygen in G is at atmospheric pressure. After allowing time for it to acquire the temperature of the water in E its volume is carefully measured.

Introduction and measurement of the hydrogen. A long rubber connecting tube is attached to a hydrogen generator, and when the issuing hydrogen is free from air, the free end of the tube is attached to K. C is at once opened, and enough

hydrogen is passed in to about double the volume of the gas already in the tube. The mixed gases are brought to atmospheric pressure as before and the volume is carefully measured.

Explosion of the mixed gases, and measurement of residual gas. All the taps being closed, wires from an induction coil are attached to the loops on the explosion tube, and a spark is passed through the mixed gases. An explosion at once takes place, and after allowing five minutes for the residual gas to reach the temperature of the water in E, the pressure in the tube is brought to that of the atmosphere and the volume of the residual gas is measured.

The reservoir having been raised, a burning match is placed at K and the tap c is opened; if the match burns more brightly the escaping gas is oxygen, otherwise it is hydrogen.

LABORATORY RECORD. Diagram of the *actual* eudiometer; enter results thus:—

	Observed volume.	Volume left.	Volume used.
Oxygen . .	x c.c.		
Mixed gases .	y c.c.		
Hydrogen .	$(y-x)$ c.c.		

- Questions* :—(i) Why is it necessary to close all taps before exploding the gas?
- (ii) What volume of hydrogen combines with one volume of oxygen?
- (iii) What contraction takes place on account of combination of (a) each c.c. of oxygen, (b) each c.c. of hydrogen?
- (iv) Under what circumstances would it be necessary to know the temperature and the height of the barometer?

*Exp. II. To find the volume of steam formed when oxygen and hydrogen combine.

Required:—As in Exp. 10; flask of amyl alcohol, and means for condensing it.

In Exp. 10 the explosion tube was kept cold, and the steam formed condensed to water. The volume of the water was so small that it was neglected.

To measure the volume of the steam, the explosion tube must be kept above 100°C . This can be done by emptying out the water from E (Fig. 59), passing the vapour of amyl alcohol through the jacket, and subsequently condensing it. This alcohol boils at 130°C .

Hydrogen and oxygen are introduced as before, but exactly 2 c.c. of hydrogen for each c.c. of oxygen.

[This may be conveniently done by using the mixed gases obtained by the electrolysis of water containing barium hydroxide as electrolyte. This mixture is called *electrolytic gas*.]

The amyl alcohol is boiled, and time allowed for the whole explosion tube to get warmed to the temperature of the vapour.

The mercury is levelled and the volume of the mixed gases read. Then the taps are turned off and the spark passed.

On re-levelling the mercury it is found that the residual gas (which is wholly steam) occupies $\frac{2}{3}$ the volume of the mixed gases taken. Hence, if the mixed gases at 130°C . occupy 30 c.c., the steam formed at 130°C . occupies 20 c.c. Of the 30 c.c. we know that 20 c.c. is hydrogen and 10 c.c. is oxygen, and these form 20 c.c. of steam. In general terms the result is:—

2 vols. hydrogen + 1 vol. oxygen = 2 vols. steam.

*Question:—*Since 3 vols. of the mixed gases produce only 2 vols. of steam, account for the necessity for closing the taps A and B to prevent ejection of mercury during the explosion.

* Demonstration.

Eudiometric analysis of air. The proportion by volume of oxygen in a given volume of air may be ascertained by modifying Exp. 10 as follows:—Introduce a convenient amount of air into G, equalize the pressure and read the volume. Then introduce *more* than enough hydrogen to combine with the oxygen in the air. Read the volume of the mixture, explode and find the volume of the residue (nitrogen and excess of hydrogen). The pressure is equalized before each volume measurement. If A is the volume of air taken, B of the mixed gases, and C of the residue, then the diminution in volume due to the explosion is $B - C$. Now this diminution is due to the combination of *all* the oxygen with twice its volume of hydrogen to form liquid water which occupies a negligible space. Hence one-third of the diminution is the volume of the oxygen, i. e.—

$$\begin{aligned}\text{Volume of oxygen} &= \frac{B - C}{3} \\ \text{Volume of nitrogen} &= A - \frac{(B - C)}{3}\end{aligned}$$

Notice that the *volumetric composition of water is assumed*, and forms the starting-point of the calculation.

QUESTIONS ON CHAPTER XIII.

1. Describe the usual laboratory method of preparing and collecting hydrogen, together with four experiments to illustrate its properties.
2. What soluble solid is obtained when sulphuric acid reacts with zinc? How is it obtained in crystals and how is it identified? In what other way can the same crystals be made?
3. Give an account of the action (if any) of (a) concentrated, (b) diluted sulphuric acid on magnesium, lead, iron, copper, and zinc.
4. What is meant by *diffusion of gases*? Describe experiments to show the diffusive power of hydrogen.
5. Describe an experiment to show that there is mutual diffusion between a light and heavy gas separated by a porous partition.

6. State Graham's law of diffusion.

Compare the rates of diffusion of oxygen and hydrogen, the density of the former being sixteen times that of the latter.

7. A certain gas has a density of 36, relative to hydrogen. Compare its rate of diffusion with that of hydrogen.

8. The rates of diffusion of carbon dioxide and air are at 0.812 : 1. Calculate the ratio of the densities of carbon dioxide and air.

9. Draw a diagram of a Kipp generator fitted up for supplying pure *dry* hydrogen. How is acid spray removed? Write notes in explanation of the diagram.

10. How can you prove that water is formed when hydrogen burns in air? What precautions are necessary to ensure that the water formed is really the result of the combustion?

11. Briefly describe how hydrogen is caused to react with (a) chlorine, (b) copper oxide. Name the substances formed. How may copper oxide be used to test for the presence of combined hydrogen in certain solids?

12. Give a full account of a method for determining the gravimetric composition of water, with notes on any errors liable to be made.

13. Account for the difference between the action of sulphuric acid on (a) pure, (b) common zinc. How can you show that common zinc contains traces of other metals?

14. Give a description of a simple voltaic cell, and state how the presence of a current can be detected.

15. State the best conditions for the action of sulphuric acid on zinc, and give some explanation of them.

16. Explain the terms:—negative plate of a cell, local action, polarization. How are the last two prevented?

17. Give evidence for the existence of nascent hydrogen.

18. Draw a descriptive diagram of a voltameter in which water is being electrolysed. Describe, in detail, how the process is performed.

19. Explain the expressions 'conductors of the first class' and 'conductors of the second class'. Give three examples of each.

20. What are electrolytes and non-electrolytes? Give examples of each and shortly describe experiments which illustrate the difference between them.

21. Explain the following terms:—anode, kathode, anion, kation, positive and negative electrodes, electrolysis.

22. Draw a diagram of a eudiometer, and describe how it is used for the determination of the composition of water by volume.

23. Is oxygen soluble in water? State the evidence for your answer. Why does the eudiometer give more accurate results for the volumetric composition of water than the voltameter?

24. Calculate the percentage volumetric composition of water from the following results obtained with a eudiometer. All the volumes are at the same temperature and pressure.

Oxygen taken = 9.5 c.c.

Oxygen and hydrogen . = 55.7 c.c.

Residual gas = 27.1 c.c.

25. Assuming a knowledge of the composition of water by volume, calculate its composition by *weight*, given that 1 l. of hydrogen at S.T.P. weighs 0.0896 g. and 1 l. of oxygen 1.4303 g., under the same conditions.

26. How can it be shown that when 1 volume of hydrogen combines with oxygen, 1 volume of steam is produced?

27. Describe how the eudiometer may be used to find the percentage volume of oxygen in air, assuming that the volumetric composition of water is known.

28. Give an account of hydrogen as a reducing agent. Draw up a list of common oxides which (a) can, (b) cannot be reduced by heating in a current of hydrogen.

29. Mention briefly how hydrogen can be obtained (a) from acids, (b) from water by the action of three metals, (c) from water without the interaction of a metal.

30. Draw up summaries of the chief (a) physical, (b) chemical properties both of hydrogen and hydrogen oxide.

CHAPTER XIV

EQUIVALENT WEIGHTS

GRAVIMETRIC LAWS OF COMBINATION

Law of definite proportions. In the experiment made to determine the composition of water by weight (p. 213) an indefinite amount of hydrogen was passed over an unknown weight of copper oxide. The result was

$$\frac{\text{Wt. of oxygen in water}}{\text{Wt. of hydrogen in water}} = \frac{8}{1} = 8.$$

This result is independent of the quantities of either hydrogen or copper oxide actually present, provided that there is enough of each to guard against excessive experimental error.

If another oxide, say lead oxide, be used as a source of oxygen, the same result for the composition of water is obtained. The conclusion to be drawn from these facts and many others of a similar nature is, that in whatever way water may be formed its composition is constant or definite. If too much of one substance is present, it is left over and not used. In no way whatever can the gravimetric composition of water be varied outside the limits of experimental error.

What is true for water is found to be true for all other substances. The accumulated facts are summarized in the *general statement* or *law* called **the law of definite proportions**, viz. **the same compound, however it has been made, always contains the same elements combined in the same proportions by weight.**

Later on, when more knowledge has been gained of the various methods of making a given compound, many illustrations of this law will be available. When we know how to find the gravimetric composition of the compound, all that is required is to analyse the compound, made in two or three different ways, in order to show that the gravimetric composition of each specimen is the same.

Exp. I. To determine the gravimetric composition of an oxide by reduction in hydrogen or coal-gas.

Required:—Pure dry cupric oxide, porcelain boat, hard-glass tube, corks, &c.

DIRECTIONS. This method can be used for any oxide which is reduced by heating in hydrogen. Coal-gas which contains over 50 per cent. of hydrogen can be used instead. It is not necessary to dry or purify either gas unless compounds of sulphur or arsenic are present.

Fit up a hard-glass tube with a singly-bored cork at each end. Through one cork place a piece of straight glass tube to connect with the gas supply, and through the other a right-angled exit-tube. See that it is all air-tight, and clamp horizontally above a Bunsen lamp. Weigh the boat (*a*) empty, (*b*) nearly filled with *pure recently dried* copper oxide.

Carefully push the boat into the hard tube without spilling any solid. Replace the cork and turn on the gas gently *without heating*. After allowing time for the expulsion of air, collect some of the gas from the exit-tube and test it as usual (see p. 209). Then light the gas at the exit-tube and heat the boat until the oxide is completely reduced to metal. Allow it to cool in a current of gas. Withdraw the boat with a piece of wire and reweigh.

LABORATORY RECORD. Arrange weighings in a schedule, showing weight of oxide taken and weight of metal left.

Questions:—(i) What is the weight of oxygen in the oxide used?

(ii) What is the percentage weight of (*a*) oxygen, (*b*) copper in black oxide of copper?

(iii) Why is it essential to have *pure dry* copper oxide?

(iv) Why is it unnecessary to have pure dry hydrogen?

(v) Why is the reduced copper cooled in an atmosphere of hydrogen (or coal-gas)?

Equivalent weights of elements. The numerical result of the gravimetric composition of water may be conveniently stated in percentages, i.e. from the actual figures obtained we can calculate the weights of hydrogen and oxygen in 100 parts by weight of water, thus:—

$$\text{Wt. of hydrogen} = 11.11 \text{ units}$$

$$\text{Wt. of oxygen} = 88.89 \text{ units}$$

$$\text{Wt. of water} = 100.00 \text{ units}$$

Another way which has been found to be still more convenient is to calculate the result for one unit of weight of hydrogen, thus:—

$$\text{Wt. of hydrogen} = \frac{11.11}{11.11} = 1 \text{ unit}$$

$$\text{Wt. of oxygen} = \frac{88.89}{11.11} = 8 \text{ units}$$

$$\text{Wt. of water} = \frac{100}{11.11} = 9 \text{ units.}$$

That weight of an element which combines with unit weight of hydrogen is called **the equivalent weight (E.W.)** of the element. Thus the equivalent weight of oxygen is 8.

The utility of this mode of expressing the results is apparent when the analyses of a large number of other compounds are available.

For example, the analysis of black oxide of copper (p. 234) can be stated:—

<i>Percentage Figures.</i>		<i>E.W. Figures.</i>
Wt. of copper	= 79.87	$= \frac{79.87}{20.13} \times 8 = 31.74$
Wt. of oxygen	= 20.13	$= \frac{20.13}{20.13} \times 8 = 8.00$
Wt. of copper oxide	= 100.00	$= \frac{100}{20.13} \times 8 = 39.74$

Since 8 wt. units of oxygen combine with 1 wt. unit of hydrogen, and 8 " " " " " " 31.74 wt. units of copper, \therefore 31.74 " " " copper are equivalent to 1 wt. unit of hydrogen, i.e. 31.74 is the E.W. of copper in black copper oxide.

By expressing the results of analyses in terms of equivalent weights a great many simple numerical relationships between the combining weights of elements have been found, and these are explained by a general theory of chemistry—the atomic theory—which will be introduced in the next chapter.

Methods for determining equivalents of elements. The method to be employed for any given element depends on the nature of the compounds it forms, and on skill in devising a scheme for obtaining accurate quantitative results.

(1) *Synthesis of hydride.* If the element forms a compound with hydrogen, the most direct way is to devise a gravimetric experiment resulting in the formation of the compound. If two out of the three substances can be weighed we shall have all the data required. This was done in the case of oxygen (p. 213); the weights of the oxygen used and of the water formed were determined, while the weight of hydrogen was found by subtraction.

(2) *Analysis of oxide.* If the element does not combine with hydrogen, as is the case with most metals, or if the ✱hydride is unstable and difficult to deal with, the indirect ✱method of analysing its oxide is used. The weight of the element which combines with 8 weight units of oxygen is taken as its E.W., e.g. the case of copper (p. 235).

(3) *Volumetric composition of gases, knowing the densities.* The E.W. of oxygen could have been deduced from the results of the volumetric synthesis of water (p. 228) if the density of oxygen had been known. [By the term **density of a gas** in chemistry is meant *the weight of any convenient volume of it divided by the weight of an equal volume of hydrogen at the same temperature and pressure.* In other words, the density of a gas (or more properly the *relative density*) is the number of times the weight of a given volume of it is greater than the weight of the same volume of hydrogen under the same conditions. For example, the density of oxygen is 16, i.e. one litre of oxygen weighs

✱ @ Metal — Nitrate ^{HEAT} Oxide
 @ oxide — Reduce to metal.

sixteen times as much as one litre of hydrogen, under the same conditions of temperature and pressure. The density of hydrogen is taken as 1 because it is the lightest substance known.]

Hydrogen.		Oxygen.	
2 vols.	combine with 1 vol.		forming water (p. 228).
$\therefore 1 \times 2$ wt. units	„ „	16×1 wt. units	„ „
$\therefore 1$ wt. unit	combines with 8	„ „	„ „
\therefore the E.W. of oxygen is 8.			

Another illustration of this method may be taken from the case of sulphur. It will be shown in Chap. XXII that sulphur combines with hydrogen, and that when 1 vol. of hydrogen sulphide gas is decomposed, 1 vol. of hydrogen is obtained. The density of the sulphide is 17. Hence—

Hydrogen sulphide.		Hydrogen.		Sulphur.
1 vol.	=	1 vol.	+	(solid)
$\therefore 17 \times 1$ wt. units	=	1×1 wt. units	+	? wt. units
$\therefore 17$ „	=	1 wt. unit	+	16 „
i.e. E.W. of sulphur is 16.				

A further illustration of the method is given in the next experiment—the determination of the E.W. of the element chlorine.

(4) *Displacement of hydrogen from an acid.* Metals like iron, zinc, magnesium, &c., do not form hydrides, but they replace hydrogen in certain acids. Exp. 3 will show how the E.W. of magnesium can be found by basing a quantitative experiment on this type of chemical action.

(5) Many other methods, some of which will be noticed later.

A hydride is a compound of an element with Hydrogen only. e.g. H_2O . HCl . NH_3 . (Ammonia)

***Exp. 2. Volumetric synthesis of hydrochloric acid gas.**

Required:—Tall cylinder, hydrogen, chlorine, as in Fig. 60.

The object of the experiment is to find the proportion by volume in which hydrogen unites with chlorine, and to ascertain the volume of hydrochloric acid gas produced.

It has been found that the gases will unite without heating, if they are exposed to a very bright light, e. g. sunlight, the electric arc light, or the light of burning magnesium. Much heat is generated and a strong vessel is required to withstand the momentary increase of pressure.



A glass tube as shown in Fig. 60 is used. It is divided by a stop-cock into two parts, AB and BC, the volume of the latter being twice that of the former. (It is not necessary that BC should be exactly twice the capacity of AB, but the ratio of the volumes should be known.)

Close the tap B and fill AB with pure chlorine; put in the stopper A. Fill BC with hydrogen and close C.

Open the tap and expose the tube to light until no green colour is visible. (Since diffusion is slow it may be necessary to leave the tube till the following lesson. In this case, the temperature and pressure should be noted on each occasion.)

Place one end (C) of the tube in a trough of mercury and remove the stopper. **Note** whether there is any contraction.

Place water over the mercury in the trough and allow it to enter the tube. **Note** how far the water rises.

(To equalize the pressure, transfer to a deep cylinder of water; adjust the tube till the water is at the same level inside and outside. Mark the level.)

Remove the upper stopper and test the gas for hydrogen.

Pour out the liquid and test it for hydrochloric acid.

* Demonstration.

LABORATORY RECORD. Record volumes and calculate thus:—

Vol. of chlorine taken	= (W) c.c.	Vol. of chlorine used	= (W) c.c.
„ „ hydrogen „	= (X) c.c.	„ „ hydrogen „	= (X - Z) c.c.
„ „ hydrochloric acid formed and dis- solved in water	= (Y) c.c.	„ „ hydrochloric acid gas formed	= (Y) c.c.
„ „ residual hydrogen	= (Z) c.c.		
<hr/>			
Vol. of chlorine	$\frac{W}{X - Z}$	Vol. of chlorine and hydrogen	$\frac{W + X - Z}{Y}$
Vol. of hydrogen		Vol. of hydrochloric acid	

Questions:—(i) What volume of chlorine combines with 1 c.c. of hydrogen?

(ii) What volume of hydrochloric acid results from the combination of 1 c.c. of hydrogen with chlorine?

(iii) In case the experiment is not completed on the same day, why is it necessary to note the temperature and pressure on both days? If the temperature is greater and the pressure less on the second day, how would this affect the result, and what corrections must be made?

Equivalent weight of chlorine. Accurate experiments show that the density of chlorine is 35.5, of hydrogen chloride 18.25, and that the result of the volumetric synthesis is—

Chlorine.		Hydrogen.		Hydrogen chloride.
1 vol.	+	1 vol.	=	2 vols.
<hr/>				
∴ 35.5 × 1 wt. units	+	1 × 1 wt. units	=	18.25 × 2 wt. units
∴ 35.5 „	+	1 wt. unit	=	36.5 „
∴ the E. W. of chlorine is 35.5.				

Exp. 3. To find the equivalent of magnesium by the displacement of hydrogen from an acid.

Required:—Magnesium ribbon, emery-paper, glass tube (about 25 mm. diam., 40 cm. long), &c., as in Fig. 61; thermometer, burette, rubber band, tall gas-jar, sulphuric acid, hydrochloric acid (strong); watch-glass.

The object of the experiment is to dissolve a known weight of magnesium in acid, to collect the hydrogen in a tube and to find its volume. The volume is reduced to S.T.P. and the weight of the gas calculated by proportion—the weight of 1 litre of hydrogen being known.

DIRECTIONS. Clean a short length of magnesium ribbon with emery-paper. Weigh a watch-glass; then place the ribbon on it and weigh out *not more than* 0.13 g., cutting off any excess above this.

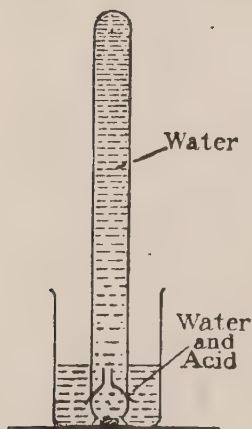


FIG. 61.

Precautions:—(a) 0.13 g. is about the maximum weight for a tube of 150 c.c. capacity. (b) The weighing should be done very carefully, *using a rider*.

Put the magnesium in a wide beaker and invert over it the head of a small thistle funnel, the stem of which has been drawn out to provide a narrow exit.*

Carefully *fill* the beaker and then the long tube with water. Invert the latter over the open end of the funnel as in Fig. 61. Pour out three-quarters of the water in the beaker and clamp the long tube vertically.

Add half a test-tubeful of strong hydrochloric or sulphuric acid† to the beaker. **Note** the effect after a few minutes.

* Or the magnesium may be wrapped in one layer of muslin tied with thread.

† Some should use hydrochloric acid, and some sulphuric, in order to compare the results.

Add more acid if necessary, and allow the apparatus to remain until effervescence ceases. Slip a rubber band over the tube, fill the beaker with water, and transfer the tube, with its contents, to a deep gas-jar.

Hold the tube (*by means of a strip of paper bent round it or a clamp*) and adjust its height until the water-level is the same inside as outside. Place the rubber band to mark this level.

Take the tube out of the jar and find its volume up to the band by means of a burette. **Note** the volume carefully.

Note the barometer reading, the temperature of the water in the jar, and the pressure of water vapour at this temperature by reference to the tables in the appendix.

LABORATORY RECORD. Enter your results thus:—

Wt. of magnesium + watch-glass	=	— g.
Wt. of watch-glass alone	=	— g.
∴ Wt. of magnesium used	=	— g.
Barometer reading	=	— mm.
Thermometer reading	=	— °C.
Pressure of water vapour	=	— mm.
Apparent vol. of hydrogen under above conditions	=	— c.c.

Calculate (i) the volume which the dry hydrogen would occupy at S.T.P. (see p. 71).

(ii) The weight of the hydrogen, assuming that 1 litre of hydrogen at S.T.P. weighs 0.09 g. approx. (0.08988 g. exactly). Then E. W.

$$\text{of magnesium} = \frac{\text{wt. of magnesium used}}{\text{wt. of hydrogen displaced}} = \text{—}.$$

Questions:—(i) Why is it important to avoid taking a large quantity of metal?

(ii) Why is it necessary to use the rider on the balance?

(iii) Why is it better to weigh the magnesium on a watch-glass and to subtract the weight of the latter, rather than to weigh the magnesium by itself?

(iv) Would an error (a) of 0.005 g. in the weight of the metal, or (b) of 5 c.c. in measuring the volume of the hydrogen, make the greater difference to the result?

- (v) What is the object of making the exit of the funnel small, or of wrapping the metal in muslin?
- (vi) Why does some time elapse between the addition of the acid and the first sign of effervescence?
- (vii) Why is the level of the water made the same inside and outside the tube before fixing the rubber band?
- (viii) Why is no attempt made to weigh the hydrogen directly?

PROBLEMS * (XIV. 3). 1. Determine the equivalent of zinc, using not more than 0.3 g. of *pure zinc-foil* and hydrochloric acid.

2. Determine the equivalent of iron, using 0.3 g. of clean *iron wire* and hydrochloric acid.

Compare this result with that obtained by the reduction of iron oxide (Prob. 1, p. 211).

3. Using about 0.12 g. of *aluminium-foil* and hydrochloric acid, as in Exp. 2, determine the weight of aluminium necessary to displace 22.2 litres of hydrogen at S.T.P.

* The weights given are for a tube of 150 c.c. capacity.

Exp. 4. To find the equivalent of magnesium by the synthesis of its oxide.*

Required:—As in Exp. 1, p. 78.

DIRECTIONS. Proceed exactly as in Exp. 1, p. 78, taking every precaution against losing much oxide as smoke.

A better result will be got by using a crucible in which magnesium has already been heated, and which is therefore blackened inside on the base. The reason is that the metal attacks the very hot porcelain and the increase of weight due to addition of oxygen is consequently less than it should be. When the base is already blackened the porcelain is protected from further action with the magnesium.

The air should only be admitted in very small quantities by *slightly* raising one side of the lid at intervals.

Allow it to cool, moisten the ash with two drops of water, warm again *gently* to drive off excess of water, and finally heat it strongly. Cool and weigh. The object of the water is to convert any yellow magnesium nitride (see p. 115) which may be formed into the oxide.

LABORATORY RECORD. Enter your results as on p. 79.

Calculate the E. W. of magnesium with reference to (a) oxygen, (b) hydrogen, assuming the equivalent of oxygen to be 8.

Compare the latter result with that obtained in Exp. 2.

* If a good result was obtained in Problem 2, p. 81, this experiment may be omitted. In this case, use the data previously obtained for the present purpose.

Exp. 5. To determine the gravimetric composition of cuprous sulphide.

Required:—Crucible (oo) and lid, pure copper powder (reduced from copper carbonate), sulphur, balance, &c.

DIRECTIONS. Weigh a clean crucible and lid, *using a rider*. Add about 1.5 g. of copper and reweigh. Then add about the same weight of powdered sulphur, and stir with a glass rod, being careful not to lose any copper. Place the covered crucible on a triangle supported at a convenient height on the ring of a retort-stand. Heat *very gently* at first. When the action is over, heat strongly for 5 min. or longer if on removing the lid the excess of sulphur is not expelled. Burn off any sulphur on the lid. Cool the covered crucible in a desiccator and reweigh.

LABORATORY RECORD. Observations on the experiment. Enter results thus:—

Wt. of crucible + lid + copper	=	— g.
Wt. of crucible + lid	=	— g.
Wt. of copper taken	=	— g.
Wt. of crucible + lid + cuprous sulphide	=	— g.
Wt. of crucible + lid	=	— g.
Wt. of cuprous sulphide formed	=	— g.

Calculate (a) the percentage composition of the sulphide;
 (b) the wt. of copper which has combined with 16 g. of sulphur, i.e. with an E.W. of sulphur.

Exp. 6. To determine the gravimetric composition of cupric sulphide.

Required:—Pure cupric sulphide, and as in Exp. 5.

DIRECTIONS. Copper forms two compounds with sulphur—called cuprous and cupric sulphides. Cuprous sulphide is made as in Exp. 5. Cupric sulphide is precipitated when hydrogen sulphide gas is passed into a solution of copper sulphate. On heating it loses sulphur and becomes cuprous sulphide. The object of the present experiment is to determine how much sulphur a given weight of cupric sulphide does lose. From these figures, combined with those of Exp. 5, the gravimetric composition of the cupric compound can be deduced

Into a crucible (previously weighed with its lid) place about 1 g. of dry cupric sulphide and reweigh, *using a rider*.

Cover the crucible and heat it as in Exp. 5 until no more sulphur is expelled. Cool in a desiccator and weigh. Reheat for a short time and weigh again when cool. Continue till two consecutive weighings agree.

LABORATORY RECORD. Observations on the experiment.

Enter weighings as in Exp. 5, showing weight of cupric sulphide taken and weight of cuprous sulphide left after heating.

Calculate (a) the weight of sulphur expelled by heat;

(b) the weights of copper and sulphur in the cuprous sulphide left, using results of Exp. 5;

(c) the total weight of sulphur in the cupric sulphide taken;

(d) the percentage composition of cupric sulphide;

(e) the weight of copper in cupric sulphide which is combined with 16 g. of sulphur;

(f) the ratio of (b) in Exp. 5 to (e) above.

The two equivalents of copper and of other metals.

Accurate analyses of the two sulphides of copper give the following figures:—

	Sulphur.	Copper.
CUPROUS SULPHIDE	20.13 %	79.87 %
or	16	$\frac{79.87}{20.13} \times 16$
i.e. in E. W.'s.	16	63.5
CUPRIC SULPHIDE	33.51 %	66.49 %
or	16	$\frac{66.49}{33.51} \times 16$
i.e. in E. W.'s.	16	31.75

Hence the E. W. of copper in cuprous sulphide (63.5) is just double the E. W. of copper in cupric sulphide (31.75). The same figures are obtained by the analyses of cuprous and cupric oxides by the method of Exp. 1 (p. 234).

This method gives the following results for oxides of lead and iron when calculated for an equivalent weight of oxygen in each compound.

	Oxygen.	Lead.
Yellow lead oxide	8	103.2
Brown „ „	8	51.6

In this case also the weights of metal combined with the same weight of oxygen are in the ratio 2 : 1.

	Oxygen.	Iron.
Magnetic iron oxide	8	20.952
Red „ „	8	18.624

Here there is no obvious simple relation between the equivalents of iron, but if the highest common factor be calculated we get 2.328.

$$\text{Now } 20.952 = 2.328 \times 9$$

$$\text{and } 18.624 = 2.328 \times 8$$

∴ the ratio of these equivalents of iron is 9 : 8.

This is an illustration of one of the more difficult cases.

Law of multiple proportions. The simple numerical relation which exists between the two equivalents of copper, &c., is found to be general for all elements which combine with another to form two or more compounds. The facts are summarized in a generalization called the law of multiple proportions, viz. if an element has more than one equivalent, the higher will be a simple multiple of the lower, or all the equivalents of the element will be simple multiples of a common factor.

The truth of this statement was first demonstrated by John Dalton of Manchester in 1803. It is known also as the second law of chemical combination.

Law of reciprocal proportions. In Exp. 3, p. 241, the E.W. of magnesium was found to be 12,

i.e. 12 g. of magnesium displace 1 g. of hydrogen from acids.

Now 8 g. of oxygen combine with 1 g. of hydrogen; what will be the ratio of the weights of magnesium and oxygen in magnesium oxide?

Exp. 4, p. 243, shows that $\frac{\text{wt. of magnesium}}{\text{wt. of oxygen}} = \frac{12}{8}$.

This holds good in all chemical changes, viz. that elements combine with one another in weights which represent the ratios of their equivalents. When one element has two equivalents this statement requires to be modified by adding the words 'or a simple multiple or sub-multiple of this ratio'. The same is true for groups of elements, i.e. radicals in double decomposition.

The generalized statement is called the *law of equivalence* or law of reciprocal proportions, viz. the ratio of the weights of any elements (or compound radicals) which enter into a chemical change is equal to the ratio of their equivalents, or is a simple multiple or sub-multiple of it.

When two elements A & B combine together in more than one proportion to produce different compounds, the different amounts of A combining with the fixed amount of B may be expressed in the ratios of small whole numbers.

Exp. 7. To examine the action of zinc and iron on copper sulphate solution; and of copper on solutions of zinc sulphate and iron sulphate.

Required:—As above; four porcelain basins, stirring rods.

DIRECTIONS. *A.* Put some strips of zinc-foil into one basin (*X*) and some clean iron filings into another (*Y*). Add cold dilute copper sulphate solution, so as to fill one-third of each basin.

Note what takes place, and stir the metals from time to time with a glass rod.

If the blue colour of the copper sulphate has entirely disappeared after about ten minutes, decant or filter the liquids into clean basins; but if not, add more metal and stir until the colour has changed.

Decant the clear liquids into clean basins; evaporate to half their bulk. Cool and add an equal volume of methylated (industrial) spirit to hasten crystallization.

Note the colour of each solution, and also the appearance of the crystals obtained. Identify the latter by comparison with crystals which you have already seen or made.

B. Take the solid residue from the basin *X*, pick out any pieces of zinc which still remain, and rinse off any dark deposit into the basin. Wash this dark deposit by decantation, and dry it in a steam-oven. Try to identify it by the flame coloration, by its action when heated in air, or any other tests which occur to you.

C. Find whether copper-foil has any action with solutions of (*a*) zinc sulphate and (*b*) iron sulphate. (Dissolve the iron sulphate in *cold* water.)

LABORATORY RECORD. Observations and results of *A*, *B*, and *C*. Description of the substances obtained.

Questions:—(i) What colour had the solid obtained in *B* and what change in colour was noticed on heating it in air?

(ii) In what respect does the result of the experiment with iron and copper sulphate differ from that with zinc and copper sulphate?

- (iii) Suggest a certain means of removing any unchanged iron or zinc from the solid residue obtained.
- (iv) Write verbal equations for the action of zinc and iron on copper sulphate?
- (v) How could this experiment be modified to determine the E. W. of zinc, knowing that of copper (63.5)?

PROBLEMS (XIV. 7). 1. Find whether there is any action between zinc-foil and *lead acetate* solution, by suspending a piece of the foil in a beaker of the solution for some days.

2. Try the action of zinc, *magnesium*, copper, or *lead* in small quantities on *silver nitrate* solution.

Displacement of metals from their salts by other metals.

The results of Exp. 7 and its problems will have shown that some metals, in the free state, are able to displace another metal from its salts, but that others have not this power. For example, zinc will displace copper from copper sulphate, but copper will not displace zinc from zinc sulphate.

Further, after such an action has taken place, the residual liquid is found to be a solution of the salt of the new metal. Thus, after zinc acted on copper sulphate, colourless crystals (identified as zinc sulphate) were obtained. The action, which is one of *replacement*, can be represented as follows:—

Zinc + copper sulphate yield zinc sulphate + copper.

It is similar to that of zinc on sulphuric acid:—

Zinc + sulphuric acid yield zinc sulphate + hydrogen.

From the facts that zinc will replace copper and lead, and lead will replace copper but not zinc, whilst copper will replace neither zinc nor lead, we conclude that zinc has a greater affinity for an acid radical than lead, and lead than copper. Hence it is possible to draw up a list of the metals in the order of their power of replacement.

Exp. 7 could be modified to determine the equivalents of metals. If a piece of zinc, of known weight, were left with excess of a solution of copper sulphate until all action was over, then, by carefully washing and weighing the copper, its equivalent with reference to zinc, and thence to hydrogen, could be calculated.

Exp. 8. To observe the effect of passing a current of electricity through solutions of metallic salts.

Required:—As in Fig. 62; beaker, 2 platinum plates soldered to copper wires; solutions of copper sulphate, sodium sulphate, and neutral litmus; nitric acid.

DIRECTIONS. *A.* Set up the apparatus as in Fig. 62, sup

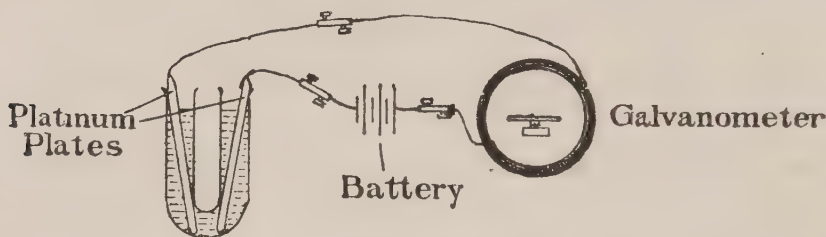


FIG. 62.

porting the U-tube in an empty beaker. Use a battery of three bichromate cells. Nearly fill the U-tube with a dilute solution of copper sulphate. Close the circuit, and **note** what takes place at the platinum electrodes.

After ten minutes remove the electrodes from the U-tube and examine them, **noting** to which pole of the battery they were attached.

B. Clean the electrodes by placing them in a little nitric acid and then rinsing with water.

Clean the U-tube, and nearly fill it with a solution of sodium sulphate covered with *neutral* litmus.

Proceed as in *A*, and **note** what happens to the litmus at the anode and the kathode, and whether there is any deposit on either of them.

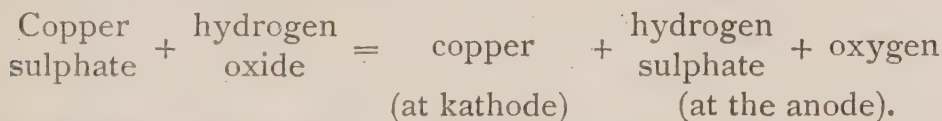
LABORATORY RECORD. Diagram of apparatus used and complete observations in *A* and *B*.

Questions:—(i) What was produced at the kathode in *A*? in *B*?

(ii) What was produced at the anode in *A*? in *B*?

(iii) Why was no sodium deposited on the kathode in *B*?

Electrolysis of aqueous solutions. (a) *Copper sulphate.* Exp. 8 has shown that copper was deposited at the kathode and that oxygen gas was evolved at the anode. It is plain that, in a chemical change between water and copper sulphate, some other product must be formed besides copper and oxygen. The hydrogen of the water and the sulphate radical of the salt have not been accounted for. These two make up sulphuric acid, and the presence of this acid at the anode can be detected as it was in the case of sodium sulphate. Hence the chemical change is :



The word **ion** is used instead of radical in describing electrolytic actions, and copper sulphate solution is supposed to consist of copper ions bearing a charge of positive electricity, and sulphate ions or *sulphions* containing the rest of the salt and bearing a negative charge.

Copper ions having a positive charge are attracted to the negative electrode or kathode. All ions which travel to the kathode are termed *kations*. Similarly the negative sulphions are attracted to the anode and are called *anions*. A copper ion has different properties to free copper owing to the electric charge; when it has given up its electricity to the kathode it becomes insoluble, and remains on the kathode in the solid state.

(b) *Sodium sulphate.* Exp. 8 shows the final products to be :

at the kathode—sodium hydroxide and hydrogen;
at the anode—hydrogen sulphate and oxygen.

Here we may suppose that there is a secondary action at the kathode between the metallic sodium and the water, resulting in the formation of sodium hydroxide and hydrogen. Otherwise the change is similar to (a). If a fused sodium salt is electrolysed in absence of water metallic sodium is formed.

(c) *Sodium hydroxide*. The only products are:

at the kathode—hydrogen; at the anode—oxygen.

The amount of sodium hydroxide in solution is the same after the action as before—in other words, only the water is decomposed. The explanation is that in a solution of the hydroxide we have sodium ions and hydroxyl ions. The former behave as in (b) and produce *sodium hydroxide* and *hydrogen* at the kathode, while the hydroxyl ions when discharged at the anode give *water* and *oxygen*. This accounts for the action of the acidic or alkaline electrolyte in the electrolysis of water.

(d) *Sulphuric acid*. This is a similar case to (c). The hydrogen ions on discharge at the kathode give free *hydrogen*, and the sulphions on discharge at the anode react with water, yielding *oxygen* and hydrogen sulphate. The amount of acid in solution therefore remains constant during the action.

Positive and negative radicals. Since hydrogen and metals form at the kathode, and are considered to have carried a positive charge as ions, they are termed electro-positive elements or radicals; conversely oxygen and acid radicals are electro-negative radicals.

Electrolysis and equivalent weights. In the electrolysis of water, hydrogen and oxygen* are produced in equivalent quantities, i.e. in the exact quantities in which they would re-combine to form water. Faraday showed that if several voltameters containing different solutions were joined in series in the same electric circuit, equivalent weights of the various substances were formed at each electrode, and also an equivalent of zinc dissolved in the battery.

Thus it is possible to determine E. W.'s by electrolysis.

Suppose we had two voltameters in a circuit, one containing

* Owing to oxygen being slightly soluble in water and to the formation of a small amount of ozone, the actual volume of oxygen collected is smaller than that really formed during electrolysis. Hence the eudiometer is more accurate than the voltameter in determining the volumetric composition of water.

acidulated water and the other copper sulphate solution. If the kathode of the latter be weighed before and after the current passes, we shall know the weight of copper deposited ; at the same time we can observe the volume of hydrogen obtained in the first voltameter, calculate its weight, and deduce the E. W. of copper by dividing the weight of copper by the weight of hydrogen.

Equivalents of compounds. From the last paragraph it will be plain that when cupric sulphate is electrolysed, for every 8 g. of oxygen produced at the anode, 31.7 g. of copper form at the kathode, 8 and 31.7 being the E.W.'s of oxygen and cupric copper respectively. The question arises as to the weight of sulphuric acid which is also produced at the anode. The chemical change at the anode results from the action of the discharged sulphion on water. Since an equivalent of oxygen is liberated from the water, an equivalent of hydrogen must have combined with the sulphate radical to form the sulphuric acid. Hence the weight of acid formed just contains an equivalent of hydrogen. It is convenient to consider that weight of an acid which contains one equivalent of replaceable hydrogen* as the *equivalent weight of the acid*. Similarly an *equivalent of an alkali or salt* is that weight of it which contains an equivalent weight of the metal.

As 49 g. of sulphuric acid and 36.5 g. of hydrochloric acid each contain 1 g. of hydrogen, the equivalent of the former is 49 and of the latter 36.5.

The E. W. of sodium is 23, and 40 g. of sodium hydroxide contain 23 g. of sodium, so that 40 is the equivalent of the hydroxide. 58.5 g. of sodium chloride contain 23 g. of sodium, hence 58.5 is the equivalent of this salt.

One equivalent of an acid will just neutralize one equivalent of a base producing one equivalent of a salt.

* Since some acids contain some hydrogen which cannot be displaced by a metal, it is usual to distinguish that which can be displaced as 'replaceable hydrogen'. In equivalents it is replaceable hydrogen which is always meant.

Exp. 9. To find the volume of an acid solution required to neutralize a known volume of an alkaline solution.

Required:—Diluted solutions of hydrochloric acid, sodium hydroxide, neutral litmus, methyl-orange, and phenolphthalein; burette, 10 c.c. pipette, glass rod, two porcelain basins, funnel.

DIRECTIONS. A. Rinse out the burette with a little acid, let it drain and then clamp it *vertically* as in Fig. 63, placing a funnel at the top.

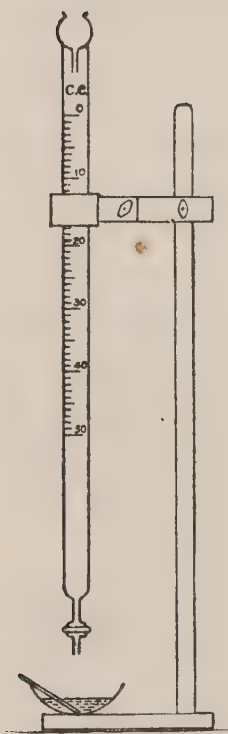


FIG. 63.

Fill the burette* with acid to a point above the zero mark, being careful that no acid runs down the outside.

Put a basin under the burette, and run out a little acid, until the meniscus is opposite some convenient mark on the scale.

Record the burette reading, making use of a card as described on p. 21.

Rinse a 10 c.c. pipette with some diluted sodium hydroxide solution, and then transfer 10 c.c. of the solution to a clean basin. (*Be careful not to get the alkali into your mouth.*)

Add a few drops of litmus solution and stir.

Place the basin about two inches below the nozzle of the burette, and run in the acid *slowly*, stirring all the time, until the litmus assumes the neutral tint.

Precautions:—Do not let the acid *splash*; take the last drop of acid from the nozzle with the stirring rod.

When you *think* you have got the neutral tint, **record** the burette reading. Add one more drop of acid, stir and judge whether the litmus was really neutral before or

* For method of using the burette and pipette see pp. 24 and 27.

not. [If not, record the reading and repeat, as often as may be necessary.]

The process of finding the volume of one solution required to exactly neutralize or react with a known volume of another solution is called **titration** (French, *titre*, a standard).

Perform three titrations, repeating any in which you accidentally added too much acid.

B. Find the effect of both acid and alkali on solutions of methyl-orange and phenol-phthalein.

Repeat *A* with each of these indicators and compare the results.

LABORATORY RECORD. Enter results thus:—

Volume of alkali solution = — c.c. Indicator used: —

1st titration.

First burette reading = — c.c. } \therefore acid used = — c.c.
Final „ „ = — c.c. }

2nd titration. ditto
and so on.

Total volume of acid used = — c.c.

Mean volume of acid used = — c.c.

Questions:—(i) Why must the burette be vertical?

(ii) Why are the burette and pipette first rinsed with the solutions of acid and alkali respectively?

(iii) What part of the meniscus is used in reading the burette?

(iv) Give reasons for the precautions.

(v) *Calculate* the volume of acid required to neutralize 25 c.c. of the alkali. Confirm by experiment, using a 25 c.c. *pipette*.

(vi) What substance is in solution after neutralization? Write a verbal equation for the action.

(vii) Compare the action of the three indicators; say which you prefer and why.

Exp. 10. To make standard solutions of (A) sodium hydroxide and (B) oxalic acid.

Required:—Corked tubes of (a) sodium hydroxide; (b) oxalic acid crystals; two standard flasks (250 c.c.), funnel, pipette.

A **standard solution** is one containing a known *weight* of substance in a litre (or other definite volume) of the *solution*. The 'strength' of a solution of a substance is usually indicated by the number of grams of substance contained in 1 litre or in 1 c.c. of the solution.

A *normal solution* (N) of an acid or alkali contains 1 gram-equivalent of the acid or alkali in 1 litre of solution. Thus 36.5 is the equivalent of hydrochloric acid, and a normal solution contains 36.5 g. of the acid in 1 litre of the solution. In 36.5 g. of this acid there is 1 g. of replaceable hydrogen.

Similarly a *deci-normal* solution $\frac{N}{10}$ contains 3.65 g. of the acid per litre. The equivalent of sodium hydroxide is 40; hence a normal solution contains 40 g. of it per litre; a deci-normal solution contains 4 g. of it per litre, and so on. 1 litre of a normal acid exactly neutralizes 1 litre of a normal alkali; or, in general terms, any volume of a standard acid solution neutralizes the same volume of a standard alkali solution of the same equivalent strength.

DIRECTIONS. A. Rinse out a 250 c.c. standard flask with water, and put a funnel in the neck. Weigh the corked tube containing the hydroxide, using the rider. Transfer about 12 g. to the flask thus:—Remove weights from the pan equal to the required weight. Incline the tube over the funnel, and by rotation and gentle tapping shake some solid into the flask.

Hold the tube mouth upwards and tap gently to make any of the solid near the edge fall back into the tube.

Put it back on the balance pan, and find whether enough has been transferred. If not, repeat until approximately the right weight has been transferred. **Record** the exact weight.

[N.B.—It is almost impossible by such a method to transfer an exact weight. All that is necessary is to get as near to it as possible, weighing *more* rather than less.]

Wash the whole of the hydroxide into the flask by means of a wash-bottle containing distilled water.

Precaution:—Do not add more water than is required to *half* fill the flask.

Cork, and shake until *all* the solid has dissolved. Fill the flask up to the containing mark, adding the last few drops with a pipette.

Cork up and label 'Solution A. . . . g. sodium hydroxide per c.c.', the strength having been found by calculation.

B. Make a standard solution of oxalic acid containing 0.063 g. per c.c. (approx.).

Calculate the weight of acid crystals required to make 250 c.c. of the solution of the above strength.

Clean the other standard flask, and having *recorded* the weight of the tube of acid crystals, transfer the right amount (or rather more) to the flask and proceed as in *A*. **Record** the final weight of the tube.

If the weight of acid dissolved was too great, a calculated additional quantity of water (beyond the 250 c.c.) must be added. The right weight of crystals for 250 c.c. is $250 \times 0.063 = 15.75$ g. Suppose 16.05 g. were actually put in. The difference is 0.3 g. Since 0.063 g. are to be

in 1 c.c., 0.3 g. should be contained in $\frac{0.3}{0.063} = 4.76$ c.c.

Make your own calculation and add this extra volume of water to the flask, using a *burette*.

Label the flask 'Solution B. . . . g. oxalic acid crystals per c.c.' [Keep both solutions for Exp. 11.]

LABORATORY RECORD. Short description, especially noting any sources of error and difficulties encountered.

Question:—What volume of water should be added to 250 c.c. of solution B (strength 0.063 g. per c.c.) to reduce the strength to (a) 0.0063 g. per c.c., (b) 0.0365 g. per c.c., (c) 0.0025 g. per c.c.?

Exp. II. To make a normal solution of sodium hydroxide.

Required :—Solutions A and B of Exp. 10; and as in Exp. 9.

The oxalic acid solution B, if properly made in Exp. 10, is a *normal* solution of oxalic acid, i. e. it contains 63 g. of oxalic acid crystals per litre, 63 being the equivalent weight of these crystals.

The solution of sodium hydroxide A is above normal strength, and the object of this experiment is first to find what its strength really is by titrating with the normal acid, then to dilute it to normal strength, and finally titrate again with the acid to find whether the dilution has been properly done. The reason that a normal solution of the alkali is not made like that of the acid in Exp. 10 is because the hydroxide may not be quite pure, and it rapidly absorbs water and carbon dioxide from the air. Hence we could never be sure of its purity. Oxalic acid crystals on the contrary can be made pure, and they do not alter in air.

DIRECTIONS. Rinse out the burette with a little of solution A and the pipette with solution B. Arrange the burette as in Exp. 9 (p. 254), and fill it up with A.

Precaution :—Keep the flask containing A corked.

Place 20 c.c. of B in a basin, using a pipette.

Add a few drops of phenol-phthalein solution to the basin.

Record the burette reading. Run A from the burette into the basin, until the pink colour is *just* permanent after stirring.

Record the burette reading.

Repeat the titrations until three concordant results are obtained. Find the mean of these three results.

To calculate the strength of the hydroxide solution :—If it is normal already, then 20 c.c. will have been used to neutralize 20 c.c. of the acid. If it is above normal strength, less than 20 c.c. will have been used; suppose the figure is 16.5 c.c.

The weight of hydroxide contained in 16.5 c.c. ought to

be contained in 20 c.c. to be normal. Therefore to make it normal add

$20 - 16.5 = 3.5$ c.c. of water to every 16.5 c.c. of solution ;

or $\frac{100}{16.5} \times 3.5$ c.c. " " " " 100 c.c. " "

[This solution was $\frac{20}{16.5}$ times normal strength.]

Use your own figures and make the calculation. Transfer 100 c.c. of solution A to a clean flask, and add the volume of water you have calculated, using a burette. **Shake well**, and having rinsed out the burette well with some of the new solution, titrate against the oxalic acid as before.

[Keep the solutions for the problems below.]

LABORATORY RECORD. Scheme of readings as in Exp. 9, p. 254. Show all the working of the calculation.

- Questions* :—(i) Assuming the purity of the hydroxide, from the figures of Exps. 10 and 11 calculate the weight of sodium hydroxide which neutralizes 63 g. of oxalic acid crystals.
- (ii) Given that 40 g. of pure sodium hydroxide is contained in 1 litre of a normal solution, calculate the percentage weight of impurity in the solid hydroxide. Make use of the result of question (i).
- (iii) Why, in making a standard solution, is it necessary to shake well after filling the flask with water up to the mark?

PROBLEMS (XIV. II). 1. Use the normal sodium hydroxide solution to make normal solutions of hydrochloric acid and sulphuric acid. Start with the ordinary dilute acids on the bench.

2. Find the ratio of the strengths of any two dilute acid solutions, being given a dilute alkaline solution of unknown strength. Calculate the strength of the stronger acid in terms of the weaker taken as unity.

QUESTIONS ON CHAPTER XIV.

[Use 0.09 g. as the weight of 1 litre of hydrogen at S.T.P.]

1. Explain carefully what is meant by the term 'equivalent weight' of an element. How may the E.W. of oxygen be found from the results of the synthesis of water?

2. Describe how the E.W. of copper can be determined, assuming that the E.W. of oxygen is 8. Give experimental details.

3. Give a full account of a method for determining the volumetric composition of hydrogen chloride. How can the E.W. of chlorine be deduced from the result?

4. How would you proceed to find the weight of zinc which displaces one gram of hydrogen from an acid?

5. Do equal weights of different metals displace equal volumes of hydrogen from the same acid?

Do equal weights of the same metal displace equal volumes of hydrogen from different acids?

6. Calculate the E.W. of zinc from the following data:—0.375 g. of zinc on solution in hydrochloric acid set free 135.3 c.c. of hydrogen, measured dry, at 15°C . and 780 mm. pressure.

7. Find the E.W. of iron, given that 0.2 g. of metal sets free 82.4 c.c. of hydrogen, measured over water, at 20°C ., the barometer standing at 750 mm. Pressure of water vapour at 20°C . = 17.5 mm. of mercury.

8. The following is the result of a gravimetric synthesis of magnesium oxide:—Weight of crucible and cover = 10.23 g.; weight of crucible and cover and magnesium = 10.38 g.; weight of crucible, cover, and magnesium oxide = 10.478 g. What is the E.W. of magnesium with reference (a) to oxygen, (b) to hydrogen?

9. Explain briefly how you could calculate the equivalent of oxygen with reference to hydrogen from the results of (a) the synthesis of magnesium oxide, and (b) the displacement of hydrogen from an acid by magnesium.

10. Explain how the gravimetric composition of cuprous and cupric sulphides can be determined.

11. State the three laws of chemical combination by weight, and illustrate each by one example.

12. Give an account of the action of zinc on a solution of copper sulphate and state how you could identify each product of the action.

13. Describe a method for passing an electric current through a solution of a salt. Compare the action of the current on solutions of copper sulphate and of sodium sulphate. How is the difference in the two actions explained?

14. How would you show that exactly equivalent quantities of sodium hydroxide and of sulphuric acid are set free at the two poles during the electrolysis of a solution of sodium sulphate?

15. How may the equivalent of copper be determined by the electrolysis of a solution of copper sulphate?

16. Explain the classification of the elements as electro-positive and electro-negative. How would you show by experiment to which class silver belongs?

17. What is a standard solution? Given a 250 c.c. flask, explain how you could make a solution of oxalic acid containing 8 g. per litre.

18. Describe a pipette, and give a clear account of the method of using it.

19. Explain carefully the construction of a burette, and mention the precautions necessary in using it.

20. What is meant by *titration*? Explain, in detail, how the process is carried out.

21. Given 100 c.c. of a solution of oxalic acid containing 0.045 g. per c.c., calculate the volume of water which should be added to reduce its strength to (a) 0.0225 g. per c.c., (b) 0.015 g. per c.c.

Given a standard solution of caustic soda, explain how it could be used to test the accuracy of your calculations.

22. Distinguish between the definitions of a *standard solution* of a solid, and the *solubility* of the solid in water.

23. Explain clearly how you could prove that the gases obtained by the electrolysis of water come from the water and not from the acid with which it is mixed.

24. Define:—(a) a normal solution of an acid, (b) equivalent weight of an acid. How would you make a deci-normal solution of oxalic acid containing 6.3 g. of acid crystals per litre?

.0375

135.3 ccs

150C

780 mm

CHAPTER XV

THE ATOMIC THEORY

Gravimetric laws of chemical combination. The experiments of Chap. XIV are typical of a large number of facts concerning the ratio of the weights in which elements combine. Since no contradictory evidence is known, the facts are summarized in three laws which are accepted as being universally true, viz. :—

- (1) *The law of definite proportions* (p. 233).
- (2) *The law of multiple proportions* (p. 247).
- (3) *The law of reciprocal proportions* (p. 247).

In order to keep these fundamental laws clearly before our minds, and to represent briefly and graphically that part of the mechanism of chemical change to which they refer, the *atomic hypothesis* has been invented. It was published by John Dalton in 1805, and makes certain simple imaginary assumptions, beyond our ability to prove, but which, if granted, show the laws to follow as logical consequences. Without the help and graphical explanation afforded by some such hypothesis the mind could not easily focus attention on the facts.

The facts themselves are, within the limits of experimental error, perfectly true, and the hypothesis is an invention of the imagination to help us to realize them. If, in future, other facts are discovered which the hypothesis cannot explain, it will require modification. Indeed, a slight modification has been made in the original statement of Dalton, and the modified hypothesis, having stood the test of time, is now known as the *atomic theory*.

The atomic theory. A statement of the theory involves two things :—

- (I) A list of the assumptions made.
- (II) An illustration of how the laws follow as consequences of the assumptions.

I. *The assumptions are—*

- (a) That an element is made up of extremely small particles called atoms (Gk. *atomos*, uncut), which remain indivisible during chemical change.
- (b) That there are as many different kinds of atoms as there are different kinds of elements.
- (c) That atoms of the same kind have the same weight, while atoms of different kinds have different weights.
- (d) That chemical combination of elements consists in the union of their atoms into groups called molecules, which hold together so long as the compound remains undecomposed.

II. *The laws of combination follow as consequences :—*

Law 1. The gravimetric composition of cuprous sulphide is constant, because the weights of the atoms of copper and sulphur are fixed, and the atoms combine in definite or fixed numbers to form a molecule of the sulphide.

Law 2. The weight of copper, combined with a given weight of sulphur in cuprous sulphide, is twice as great as that combined with the same weight of sulphur in cupric sulphide, because the same number of atoms of sulphur is combined with twice as many atoms of copper in the cuprous as in the cupric compound.

Law 3. The ratio of the weights of elements which interact chemically is equal to the ratio of their E.W.'s (or to a multiple), because the ratio of the E.W.'s is the ratio of the atomic weights (or a simple multiple).

It is convenient to assign a symbol to represent the atom of every element. A compound is represented by a group of these atomic symbols constituting a molecule. By means

of equations expressed in these symbols we have a brief and graphic means of representing chemical changes. The following are examples of atomic symbols* :—Hydrogen, H ; Sulphur, S ; Phosphorus, P ; Zinc, Zn ; Oxygen, O ; Nitrogen, N ; Iron (Ferrum), Fe ; Copper (Cuprum), Cu ; Magnesium, Mg ; Calcium, Ca.

Atomic weights. Since atoms are, by supposition, inconceivably small, it is impossible to isolate and weigh them directly. What can be done is to find the ratio of the weights in which comparatively large quantities of elements combine, and so find the weight of one element which combines with *unit* weight of another. This was the method of determining equivalent weights, and the E.W. of an element was defined as the weight of it which combined with or displaced *unit* weight of hydrogen. Hydrogen was chosen as the standard substance for comparison because its density is less than that of any other substance ; presumably its atomic weight is also less.

Now, 8 g. of oxygen combine with 1 g. of hydrogen.

If x is wt. of 1 atom of oxygen and there are n atoms in 8 g. ;
 „ y „ „ hydrogen „ m „ 1 g. ;
 then $nx = 8$ and $my = 1$.

$$\therefore \frac{nx}{my} = 8.$$

The weight of 1 atom of hydrogen is chosen as the unit for atomic weights, hence $y = 1$.

$$\therefore \frac{nx}{m} = 8; \quad \therefore x = 8 \frac{m}{n}.$$

Unless we know the value of m and n we cannot find the atomic weight (A.W.) of oxygen or of any other element.

$\frac{m}{n}$ represents the number of *atoms* of hydrogen which combine with one *atom* of oxygen to form one molecule of water.

* See Alembic Club Reprints—No. 2.

If $m = n$, then $\frac{m}{n} = 1$ and $x = 8$;

„ $m = 2n$, „ $\frac{m}{n} = 2$ „ $x = 16$;

„ $2m = n$, „ $\frac{m}{n} = \frac{1}{2}$ „ $x = 4$;

and so on.

This fraction $\frac{m}{n}$ is called the *valency* of the element, in this case oxygen. Hence,

$$\text{A.W.} = \text{E.W.} \times \text{valency.}$$

The E.W. can *always* be found, but we must be able to find the valency of an element before we can determine the A.W. The following definitions should be remembered:—

Atomic weight of an element is the number of times one atom of that element is heavier than one atom of hydrogen.

The Valency of an element is the number of atoms of hydrogen which one atom of the element combines with or displaces. It is clear that the valency must be an integer and not a fraction. If an element has two E.W.'s, e.g. copper, it will have two valencies, for an element cannot have more than *one* A.W.

E.W. \times valency for *cuprous compounds* = E.W. \times valency for *cupric compounds*
 $\therefore 63.5 \times$ „ „ „ = $31.75 \times$ „ „ „
 \therefore valency of copper in cupric compounds is twice that in cuprous compounds.

Dalton never really determined any atomic weights, though he thought he had done so. When two elements formed only one compound, he *assumed* that $\frac{m}{n} = 1$, so his atomic weights were really equivalent weights. When two different compounds containing the same elements existed, he *assumed* that $\frac{m}{n} = 1$ in one case, and that $\frac{m}{n} = 2$ in the other. This was plainly unjustifiable.

There are two principal methods now used for finding the valency of an element; one derived from the laws of gases and applicable only to gases and vapours, the other derived from a study of specific heat, applicable only to *solid* elements, with a few exceptions.

Laws of gases. I. *Charles's Law* (p. 62) states that equal volumes of *all* gases expand equally when heated under the same pressure.

II. *Boyle's Law* (p. 66) states that a given alteration in pressure changes equal volumes of *all* gases to the same extent when at the same temperature. These are very remarkable facts and point to some similarity in the structure of *all* gases, for which there is no analogy in the cases of solids or liquids. Another equally remarkable law must now be considered.

III. *Gay-Lussac's Law of volumes.* The eudiometer (p. 229) showed that—

- | | | | | |
|------------------------|---------------|--------------------|---------|----------------------------------|
| (a) 2 c.c. of hydrogen | combine with | 1 c.c. of oxygen | forming | 2 c.c. of steam. |
| (b) 1 c.c. of hydrogen | combines with | 1 c.c. of chlorine | " | 2 c.c. of hydrochloric acid gas. |

It is plain that the ratios of the combining volumes of these gases are very simple, and that the ratio of the volume of the compound gas to that of either of its constituents is also very simple. Similar simplicity is found in the ratios of the combining volumes of *all* gases, and the facts are summed up in a law formulated by **Gay-Lussac** in 1811:—**When gases combine, their volumes are in the ratio of simple whole numbers, and the volume of the product (if a gas) is also simply related to the volumes of the gases before combination.**

Here we have a law concerning combining *volumes*, just as we had laws dealing with combining *weights*. The atomic theory was invented to explain the latter, and the following theory, containing only one assumption beyond those of the atomic theory, has been invented by Avogadro (1811) to explain these laws of gases.

Avogadro's theory. Equal volumes of all gases, at the same temperature and pressure, contain an equal number of molecules.

This gives the chief assumption, but it is also supposed that the molecules of gases do not touch one another but are separated by comparatively large spaces.

By a molecule is meant the smallest particle of a gas which exists in the free state. In a compound gas a molecule must necessarily contain at least two atoms. In an elementary gas, such as oxygen or hydrogen, a molecule might conceivably contain only one atom. Reasons will be given later for the supposition that the molecules of most gaseous elements contain two atoms.

These assumptions clearly explain the three laws of gases, for if the same volumes of two gases are heated through the same range of temperature, the molecules should separate to the same extent, i. e. the expansion would be the same, and this is what Charles's Law states to be the fact. Similarly, equal increase of pressure on equal volumes should diminish the space between each molecule to the same extent, and this is what Boyle's Law affirms. Again, when two gases combine, 1, 2, 3... &c. molecules of the one should, by the atomic theory, combine with 1, 2, 3... &c. molecules of the other, i. e. the ratio of the combining volumes should be definite and simple. This is Gay-Lussac's Law.

Constitution of molecules. There can be no such thing as an atom of a compound, for by the atomic theory the smallest particle of a compound must be a group of two atoms, i. e. a molecule. In an element the smallest particle actually existing in the free state may, by the atomic theory, be a single atom or a molecule containing two or more similar atoms, i. e. a molecule of hydrogen in a mass of the gas that can be collected may be represented as H, H₂, H₃... &c. without violating the atomic theory. The question of the molecular constitution of elementary gases can only be settled by the appearance of further evidence.

Consider the volumetric composition of hydrochloric acid gas:—

By experiment, $\begin{array}{rcl} \text{hydrogen} & + & \text{chlorine} = \text{hydrochloric acid gas.} \\ 1 \text{ vol.} & + & 1 \text{ vol.} = 2 \text{ vols.} \end{array}$

By Avogadro's theory, $\begin{array}{rcl} 1 \text{ mol.} & + & 1 \text{ mol.} = 2 \text{ mols.} \end{array}$

\therefore one mol. $\left\{ \begin{array}{l} \text{hydrochloric} \\ \text{acid gas} \end{array} \right.$ contains $\left\{ \begin{array}{l} \text{hydrogen} \\ \frac{1}{2} \text{ mol.} \end{array} \right.$ and $\left\{ \begin{array}{l} \text{chlorine} \\ \frac{1}{2} \text{ mol.} \end{array} \right.$

By the atomic theory, atoms are indivisible.

$\therefore \frac{1}{2}$ mol. of hydrogen contains 1 atom at least.

$\frac{1}{2}$ „ chlorine „ 1 „ „

\therefore 1 „ $\left\{ \begin{array}{l} \text{hydrogen} \\ \text{chlorine} \end{array} \right.$ „ 2 atoms $\left\{ \begin{array}{l} \text{hydrogen} \\ \text{chlorine} \end{array} \right.$ at least.

Further, a molecule of hydrogen or chlorine cannot contain 3 atoms, for then a molecule of the acid gas would contain $1\frac{1}{2}$ atoms of each, and this violates the atomic theory.

\therefore a molecule of hydrogen is H_2 , or H_4 , or H_6 , ...

„ chlorine is Cl_2 , or Cl_4 , or Cl_6 , ...

In lack of chemical evidence to decide which of these should be taken as correct, the simplest, viz. H_2 and Cl_2 , are adopted, and confirmation of the choice is derived from physics (molecular theory of gases).

Molecular weights. Granting the above, it is clear that a molecule of hydrogen weighs twice as much as an atom; i. e. *the molecular weight (M.W.) of hydrogen is 2*. This implies that the weight of an atom of hydrogen is the unit for molecular weights as well as for atomic weights. Hence, *the molecular weight of any substance is the ratio of the weight of its molecule to that of an atom of hydrogen*.

Relative density of gases. The statement that 'the density of oxygen is 16' means that a given volume of oxygen weighs 16 times as much as the same volume of hydrogen under the same conditions. [The word 'density' is an abbreviation for 'density relative to hydrogen', or 'relative density'.]

Now the density of a gas or vapour can always be found

by experiment, hence we can always find the molecular weight of a gas, for—

$$\frac{\text{wt. of 1 vol. oxygen}}{\text{wt. of 1 vol. hydrogen}} = \frac{\text{wt. of 1 mol. oxygen}}{\text{wt. of 1 mol. hydrogen}};$$

$$\therefore \text{density of oxygen} = \frac{\text{M.W. of oxygen}}{2};$$

$$\begin{aligned}\therefore \text{M.W. of oxygen} &= 2 \times \text{density of oxygen}; \\ &= 2 \times 16 = 32;\end{aligned}$$

or, if M represents the M.W. of a gas and D is its density,

$$M = 2D.$$

Gram-atoms and gram-molecules. Experiment shows that 1 litre of hydrogen at S.T.P. weighs 0.0899 gram.

$$\therefore 1 \text{ g. hydrogen occupies } \frac{1}{0.0899} = 11.1 \text{ l. (approx.)};$$

$$\therefore 2 \text{ g. } \quad \text{,,} \quad \text{occupy} \quad 22.2 \text{ l.}$$

22.2 l. of hydrogen at S.T.P. are said to contain 1 gram-molecule of hydrogen, and 11.1 l. contain 1 gram-atom.

Similarly 22.2 l. of *any gas* at S.T.P. contain 1 gram-molecule of that gas.

Derivation of atomic weights of elements from molecular weights of their compounds. The method consists in :—

- (1) Determining the M.W.'s of as many volatile compounds of the element as possible, by ascertaining their density and doubling the figure obtained.
- (2) Analysing gravimetrically each compound and expressing the ratio of the weights of each element present in one gram-molecule of the compound.
- (3) Taking the *least* weight of the element found in a gram-molecule of any compound as the approximate value of the gram-atom of the element.
- (4) Using this approximate A.W. to find the valency, and then multiplying the E.W. determined in the most accurate way by the valency.

Case of oxygen. The following table shows the application of the method for a few of the many volatile compounds of oxygen :—

Name of Compound.	Density (by experiment)	∴ M.W. is	Wt. of oxygen in 1 gram-mol. (by experiment)	Weight of other element is (by experiment)
Steam	9	18	16	2 (hydrogen)
Oxide of sulphur (A)	32	64	32	32 (sulphur)
" " (B)	40	80	48	32 (sulphur)
" " carbon (A)	14	28	16	12 (carbon)
" " (B)	22	44	32	12 (carbon)

The table shows that 16 grams of oxygen is the smallest weight of oxygen contained in 1 gram-molecule of these compounds, and the same is true of all the known volatile compounds of oxygen.

Hence 16 g. of oxygen is the approximate weight of 1 gram-atom of oxygen, or, in other words, the atomic weight of oxygen is 16 (approx.).

The most exact E.W. for oxygen is found to be 7.88.

∴ exact A.W. of oxygen is $7.88 \times 2 = 15.96$.

In a similar manner the atomic weights of nitrogen, chlorine, carbon, sulphur, and other elements forming volatile compounds are found.

Symbol for a molecule of water. Since—

$$\text{the valency of an element} = \frac{\text{A.W.}}{\text{E.W.}} \text{ (p. 265);}$$

$$\therefore \text{valency of oxygen} = \frac{16}{8} = 2;$$

i.e. one atom of oxygen combines with two atoms of hydrogen. Hence H_2O represents a molecule of water.

If this is correct, the molecular weight (M.W.) of water is $2 + 16 = 18$.

By experiment the density of steam is 9.

∴ M.W. of steam is 18. Hence the above symbol is verified.

Molecular formula of hydrogen chloride. The density of the gas is 18.25.

$$\therefore \text{M.W.} = 18.25 \times 2 = 36.5.$$

The least weight of chlorine ever found in 1 gram-molecule of any of its volatile compounds is 35.5 g., i. e. the A.W. of chlorine is 35.5. Now, one molecule of hydrogen chloride must contain at least *one* atom of chlorine and *one* atom of hydrogen (p. 268).

But, 1 gram-atom of chlorine	weighs	35.5 g.
and 1 ,, ,, hydrogen	,,	<u>1.0 g.</u>

$$\therefore \text{the sum of these weights} = 36.5 \text{ g.}$$

and this is the weight of 1 gram-molecule of hydrogen chloride.

Hence one molecule of hydrogen chloride contains *one* atom of each element, i. e. HCl represents the molecule, and not H_2Cl_2 , H_3Cl_3 , . . .

Molecular formulae of elements. These are easily determined from the density and atomic weight found as explained, in the case of oxygen, on p. 270. Thus the density of oxygen is 16, \therefore M.W. is 32. Now, A.W. is 16, \therefore a molecule of oxygen contains 2 atoms, and is represented by the symbol O_2 . Most of the gaseous elements have di-atomic molecules, e. g. chlorine, Cl_2 ; nitrogen, N_2 .

Phosphorus vapour is represented by P_4 , and sulphur vapour consists of a mixture of S_4 and S_6 molecules at temperatures slightly above its boiling-point, but at higher temperatures they break up into di-atomic molecules, S_2 .

Zinc and mercury have mon-atomic molecules at the temperatures at which their vapour densities were determined, and their molecular formulae are identical with their atomic symbols, i. e. Zn represents one molecule of zinc vapour and also one atom of zinc.

QUESTIONS XV A.

[Use 0.09 g. as the weight of 1 litre of hydrogen at S.T.P.]

1. The equivalent of nitrogen is 4.66; what will be the simplest formula for a compound of nitrogen and hydrogen, supposing that the atomic weight of nitrogen is (a) 4.66, (b) 9.32, (c) 14?

2. The density of a compound of oxygen and sulphur is 2.217 relative to air; if the density of air is 14.43 relative to hydrogen, what is the molecular weight of the oxide of sulphur?

This compound contains 50 per cent. of each element. Calculate the weights of oxygen and sulphur in the gram-molecule of the compound; also, given that the atomic weights of oxygen and sulphur are respectively 16 and 32, find a formula for a molecule of the compound.

3. 50 c.c. of nitrogen at S.T.P. are found to weigh 0.0625 g.; find its density relative to hydrogen, and thence its molecular weight.

The gram-molecule of no compound of nitrogen is known to contain less than 14 g. of this element; what is the formula for the molecule of nitrogen?

4. 50 c.c. of a compound of carbon and oxygen, at S.T.P., are found to weigh 0.0625 g.; what is the gram-molecule of this compound?

5. Two compounds of tin and oxygen are known; *A* contains 88.06 per cent. of tin and 11.94 per cent. of oxygen, and *B* contains 78.66 per cent. of tin and 21.33 per cent. of oxygen; do these compounds illustrate the law of combination in multiple proportions?

6. By heating weighed quantities of two compounds of iron and oxygen in hydrogen, they are found to lose respectively 30 per cent. and 27.58 per cent. of their weight, metallic iron being left; calculate the equivalent of iron in each compound, and state whether they illustrate the second law of chemical combination or not.

44.00
100
27.58
72.42

Atomic weights of elements which do not form volatile compounds. The metals form very few volatile compounds, so that the foregoing method is not applicable. Originally atomic weights were assigned for various probable but inconclusive reasons; still, many of these have proved to be correct in the light of more recent knowledge.

Dulong and Petit determined the quantity of heat required to raise one gram-atom of different solid elements through one degree. This quantity they called the **atomic heat**. For the majority of solid elements they found that the atomic heat came to nearly the same number, viz. 6.4. This is summed up in the following law:—

Dulong and Petit's Law.—The atomic weight of a solid element multiplied by its specific heat is approximately 6.4, or, more briefly, the atomic heat of a solid element is 6.4 (approx.).

The procedure to determine an atomic weight by using this law is:—

- (a) Divide 6.4 by the specific heat to get the *approximate* atomic weight.
- (b) Divide approx. A.W. by E.W. to get the valency, taking the nearest whole number.
- (c) Multiply E.W. by the valency to obtain the *exact* atomic weight.

For example:—

- (a) Specific heat of copper = 0.095.

$$\therefore \frac{6.4}{0.095} = 67 \text{ (approx. A.W.)}$$

- (b) E.W. is 31.75.

$$\therefore \text{valency is } \frac{67}{31.75} = 2, \text{ to nearest whole number.}$$

- (c) Exact A.W. = $2 \times 31.75 = 63.5$.

The following is a list of some of the commoner elements,

with their symbols, approximate atomic weights, valencies, and specific heats:—

Name of element.	Symbol.	Atomic weight.	Specific heats.	Valencies.
Aluminium	Al	27	0.202	iii
Calcium	Ca	40	0.17	ii
Carbon	C	12	0.463	iv
Chlorine	Cl	35.5	—	i
Copper (Cuprum)	Cu	63.5	0.095	i and ii
Gold (Aurum)	Au	196.7	0.032	i and iii
Hydrogen	H	1	—	i
Iodine	I	127	0.054	i
Iron (Ferrum)	Fe	56	0.112	ii and iii
Lead (Plumbum)	Pb	206.4	0.031	ii
Magnesium	Mg	24	0.245	ii
Manganese	Mn	55	0.122	ii
Mercury (Hydrargyrum)	Hg	200	0.033	i and ii
Nitrogen	N	14	—	iii and v
Oxygen	O	16	—	ii
Phosphorus	P	31	0.202	iii and v
Potassium (Kalium)	K	39	0.166	i
Silicon	Si	28	0.203	iv
Silver (Argentum)	Ag	108	0.056	i
Sodium (Natrium)	Na	23	0.293	i
Sulphur	S	32	0.188	ii
Tin (Stannum)	Sn	118	0.0548	ii and iv
Zinc	Zn	65	0.093	ii

Valency. Elements having a valency = 1 are called *monads* or *monovalent* elements, e. g. hydrogen, chlorine, sodium. When the valency is 2, 3, 4, or 5, these elements are *dyads*, *triads*, *tetrads*, *pentads* or *di-*, *tri-*, *tetra-*, *penta-*valent respectively. Thus oxygen is a dyad, nitrogen a triad or pentad, carbon a tetrad element.

The valency of an element expresses the number of *hydrogen atoms* which 1 atom of the element combines with or displaces.

QUESTIONS XV B.

1. Find approximate atomic weights for elements having the following specific heats:—(a) 0.0311, (b) 0.0319, (c) 0.108, (d) 0.0523.

2. How many calories would be required to raise 100 g. of each of the following elements from 0° C. to 1° C.?—tin, potassium, iron, manganese.

3. What would probably be the specific heat of solid oxygen, supposing that this element obeys Dulong and Petit's Law?

4. 3.34 g. of a metallic oxide when heated in hydrogen lost 0.40 g., the metal being left. If the metal has a specific heat 0.0548, find its equivalent, valency, and atomic weight.

5. 2.5 g. of a metallic oxide are heated in hydrogen. 0.45 g. of water is formed; find the equivalent of the metal. The specific heat being 0.0305, calculate the atomic weight and the valency of the metal.

6. Making use of the table of valencies given on p. 274, find formulae for the oxides of sodium, zinc, iron, phosphorus; for compounds of silicon with hydrogen, of gold with chlorine, and of phosphorus with chlorine.

7. A metal having a specific heat of 0.057 forms an oxide containing 82.53 per cent. of metal. Find the equivalent weight of the metal and also its exact atomic weight.

8. One oxide of a metal *A* contains 30 per cent. of oxygen, and the oxide of another metal *B* contains 12.5 per cent. of oxygen; the specific heats of *A* and *B* are 0.1138 and 0.0567 respectively. Calculate the *exact* atomic weights of *A* and *B*.

Determination of molecular formulae of compounds. To find the *simplest* formula for a compound which shall express both its gravimetric composition and atomic composition, it is necessary to know (1) the figures giving its gravimetric analysis, (2) the A.W.'s of the elements it contains. The gravimetric analysis gives the actual *weights* of the various elements present in a stated *weight* of the compound, but the formula is to give us the number of *atoms* of each element present in one *molecule* of the compound. Hence, to find the ratio of the numbers of these atoms, the actual weight of each element given in the analysis must be divided by the atomic weight of that element. If the resulting figures are not whole numbers, *all* of them must be multiplied by some figure to effect this. Attaching these figures to the symbols of each element, we have the *simplest* formula for the compound. This is either the *true* formula or a sub-

multiple of it. To settle this point we must know its density in the gaseous state, and thus find its M.W. Then, if necessary, the simplest formula must be doubled, trebled, &c., to make the total weights of the atoms equal to the ascertained molecular weight. The following examples illustrate the procedure:—

(1) *Turpentine*. The result of gravimetric analysis is—

Carbon	88.235
Hydrogen	11.765
Turpentine	<u>100.000</u>

The atomic weight of carbon is 12 and of hydrogen 1. The ratio of the number of carbon atoms to hydrogen atoms is worked out thus:—

	Carbon.	Hydrogen.
Ratio of actual wts. by analysis	88.235	: 11.765
Ratio of number of atoms (divide above by A.W.'s)	$\frac{88.235}{12} = 7.353$: $\frac{11.765}{1} = 11.765$
Ratio of number of atoms with one integer (divide through by smallest figure)	$\frac{7.353}{7.353} = 1$: $\frac{11.765}{7.353} = 1.6$
Ratio of number of atoms in simplest integers	$1 \times 5 = 5$: $1.6 \times 5 = 8$

Hence C_5H_8 is the *simplest* formula.

The density of turpentine vapour is 68.

\therefore M.W. of turpentine is $2 \times 68 = 136$.

Now C_5H_8 corresponds to a M.W. of

$$5 \times 12 + 1 \times 8 = 68.$$

\therefore the figures in C_5H_8 must be multiplied by 2 to bring the M.W. of the formula to 136, i.e. the correct molecular formula is $C_{10}H_{16}$.

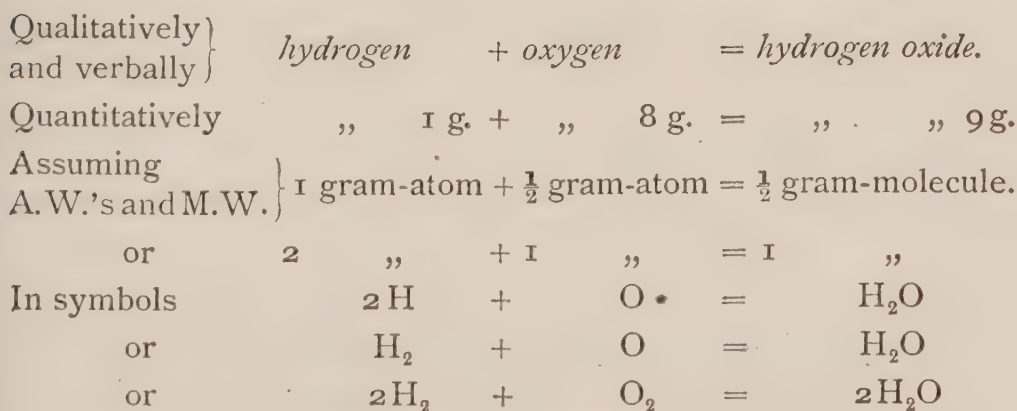
(2) *Cuprous sulphide*. The gravimetric composition (p. 244) is 20.13 per cent. of sulphur and 79.87 per cent. of copper. The A.W.'s are—sulphur, 32; copper, 63.5.

	Copper.	Sulphur.
Ratio of actual weights	79.87	: 20.13
Ratio of number of atoms	$\frac{79.87}{63.5} = 1.26$: $\frac{20.13}{32} = 0.63$
Ratio of number of atoms in integers	$\frac{1.26}{0.63} = 2$: $\frac{0.63}{0.63} = 1$

The simplest formula is Cu_2S .

Since this compound is not volatile, its vapour density is unknown, and we cannot find its true formula. In such a case the simplest formula is accepted until any evidence to the contrary appears.

Chemical equations. Verbal equations have been written in many previous experiments to represent *qualitative* chemical changes. By using atomic and molecular symbols instead of words the *quantitative* facts of the change may also be briefly expressed. Thus, considering the synthesis of water :



The last form is the most correct because oxygen gas consists of molecules each containing two atoms. The figures

in front of a molecular formula show the ratio of the combining *volumes* in the case of gases. For example, the equation



shows that the ratio of the volumes of hydrogen, oxygen, and steam is 2:1:2.

Hence, an equation for a chemical change written in molecular formulae expresses, at a glance, not only the qualitative nature of the change, but also the gravimetric relationships in *all* cases, and the volumetric relationships in the case of gases.

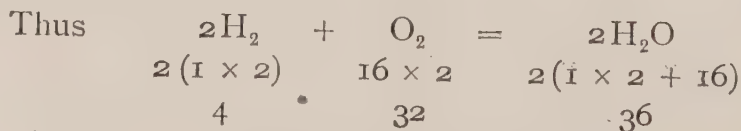
When translated into words the equation comprises the following statements:—

- (1) 2 molecules of hydrogen, each consisting of 2 atoms, combine with 1 molecule of oxygen containing 2 atoms, and produce 2 molecules of hydrogen oxide, each containing 2 atoms of hydrogen and 1 atom of oxygen.
- (2) The ratio of the weights of hydrogen, oxygen, and water is $(2 \times 2 \times 1) : (2 \times 16) : 2(2 + 16) = 4 : 32 : 36$.
- (3) The ratio of the volumes is 2:1:2, or, if the weights are taken in grams, the volumes in litres are 44.4:22.2:44.4.

Calculations involving the use of chemical equations.

Example 1. To calculate the weight of water produced when 15 g. of hydrogen are burned in air.

Write down the equation, and beneath each symbol write the weights represented by it.



Since 4 g. of hydrogen give 36 g. of water

\therefore 1 g. „ gives $\frac{36}{4}$ g. of water

\therefore 15 g. „ give $\frac{36 \times 15}{4}$ g. = 135 g. of water.

Example 2. What weight of water is produced by the combustion of 30 litres of hydrogen at S.T.P.?

It has already been seen that the gram-molecule of a gas at S.T.P. occupies 22.4 litres.

From the equation it is learnt that

2 molecules of hydrogen give 2 molecules of water.

Or 2 gram-molecules occupying at S.T.P. 2×22.4 litres give 1 gram-molecule of water, i.e. 36 g.

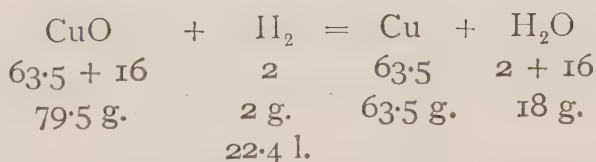
Since 2×22.4 l. of hydrogen at S.T.P. give 36 g. of water

$$\therefore 1 \text{ l.} \quad \quad \quad \text{gives } \frac{36}{2 \times 22.4} \text{ g. of water}$$

$$\therefore 30 \text{ l.} \quad \quad \quad \text{give } \frac{36 \times 30}{2 \times 22.4} = 24.1 \text{ g. of water.}$$

Example 3. What volume of hydrogen at 15°C. and 770 mm. pressure is required to reduce 50 g. of copper oxide to copper?

First write down the equation and the weights and volumes involved:



Since 79.5 g. copper oxide require 22.4 l. hydrogen at S.T.P.

$$\therefore 1 \text{ g.} \quad \quad \quad \text{requires } \frac{22.4}{79.5} \text{ l.}$$

$$\therefore 50 \text{ g.} \quad \quad \quad \text{require } \frac{22.4 \times 50}{79.5} \text{ l. at S.T.P.}$$

The volume which the hydrogen will occupy at 15°C. and 770 mm. must now be calculated. It will be (see p. 68)

$$\frac{22.4 \times 50 \times 288 \times 760}{79.5 \times 273 \times 770} \text{ litres.}$$

Example 4. What weight of copper oxide will be reduced by 15 l. of hydrogen at 17°C. and 740 mm. pressure?

The equation tells us that 79.5 g. of the oxide are reduced by 22.4 l. of hydrogen at **S.T.P.** Now before we can com-

pare two volumes of gases they must both be at the *same* temperature and pressure. Hence, before introducing these volumes into a proportion sum we must first find, *either* what volume 22.4 l. at S.T.P. will occupy at 17° C. and 740 mm., *or* what volume 15 l. at 17° C. and 740 mm. occupy at S.T.P. We may do which we like, but one *must* be done.

Choosing the first alternative,

22.4 l. at S.T.P. will be $22.4 \times \frac{290}{273} \times \frac{760}{740}$ l. at 17° C. and 740 mm.

Hence, under the given conditions of temperature and pressure—

$22.4 \times \frac{290}{273} \times \frac{760}{740}$ l. hydrogen require 79.5 g. copper oxide.

∴ 1 l. „ requires $\frac{79.5}{22.4} \times \frac{273}{290} \times \frac{740}{760}$ g. copper oxide.

∴ 15 l. „ require $79.5 \times \frac{15}{22.4} \times \frac{273}{290} \times \frac{740}{760}$ g. copper oxide.

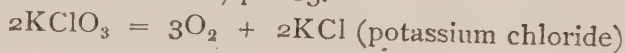
Equations for reactions involving oxygen, oxides and salts. The equations for some of the reactions considered in earlier chapters may be conveniently given here. Confirmation of some of the formulae will be found in later chapters.

Formation of oxygen.

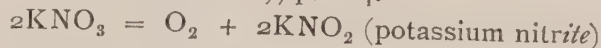
(1) From mercuric oxide, p. 96.



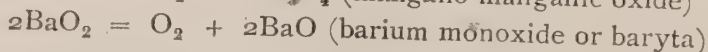
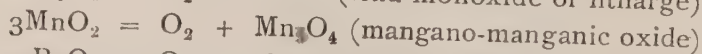
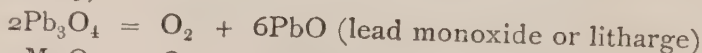
(2) From potassium chlorate, p. 105.



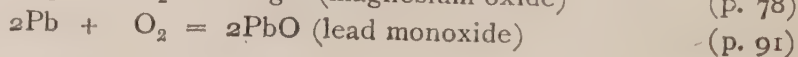
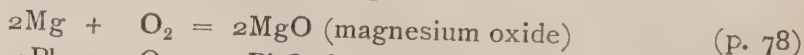
(3) From nitre (potassium nitrate), p. 104.

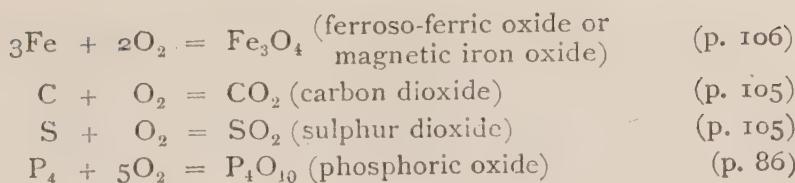


(4) From red lead and from manganese dioxide and barium dioxide (pp. 104 and 109)

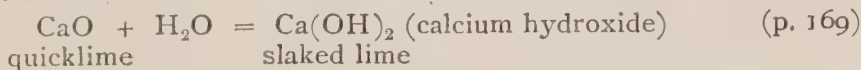


Combustion of metals and non-metals in oxygen.

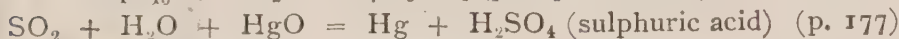
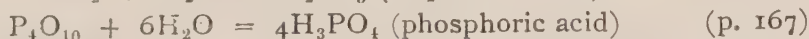
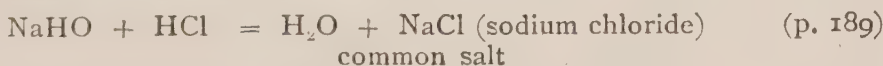
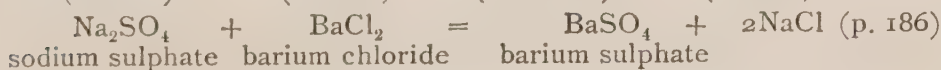
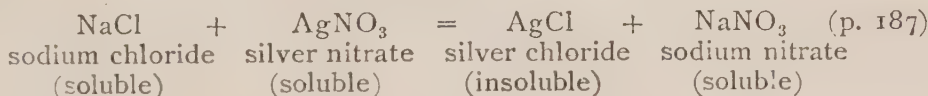
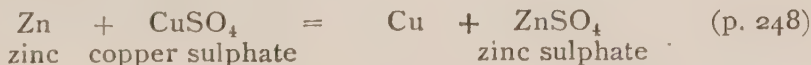
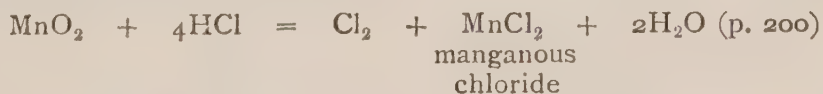


*Action of oxides on water.*

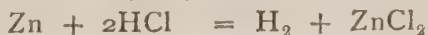
(1) Basic oxides.



(2) Acidic oxides.

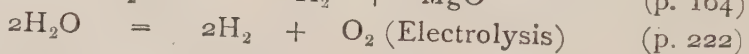
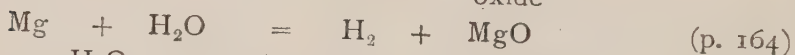
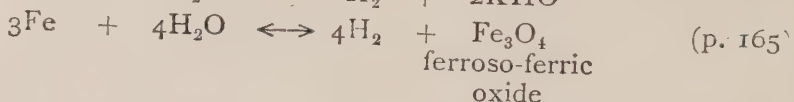
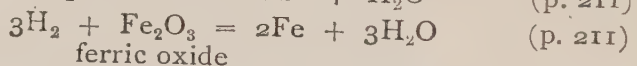
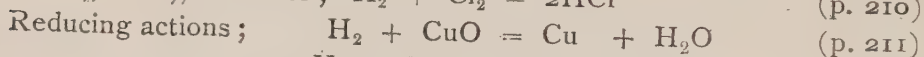
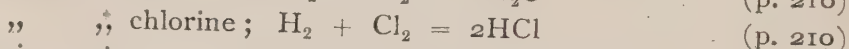
*Action of bases on acids—formation of salts.**Action of salts on salts—double decomposition.**Action of metals on salts—displacement.**Action of peroxides on hydrochloric acid.***Equations involving hydrogen.***Formation of hydrogen.*

(1) From acids.



The equations for the action of these acids on iron (Fe) and magnesium (Mg) are precisely similar.

(2) From water.

*Reactions of hydrogen.*

QUESTIONS XVC.

[Atomic weights will be found on p. 274 and in Appendix. Use 0.09 g. as the weight of 1 l. of hydrogen at S.T.P.]

1. Write out the 'Law of Constant Proportions'. 7.2 g. of a certain oxide of iron left 5.6 g. of iron on reduction; a specimen of *apparently* the same oxide (prepared in a different way) was found to contain 77.8 per cent. of iron. Have the two samples the same quantitative composition or not?

2. Write out the 'Law of Combination in Multiple Proportions'. An element forms two oxides which contain respectively 24.24 and 34.8 per cent. of oxygen. Show that these figures are in agreement with the law.

3. Two oxides of nitrogen were found to possess the following percentage composition:—

	I.	II.
Nitrogen . . .	63.64	46.67
Oxygen . . .	36.36	53.33

Are these figures in agreement with the Law of Multiple Proportions?

4. Write an account of the atomic theory of Dalton. How was it that Dalton failed to give the correct atomic weights of elements?

5. State Gay-Lussac's law of volumes. In what proportions by volume do the following gases combine, and what are the

volumes of the gaseous products?—(a) hydrogen and chlorine; (b) hydrogen and oxygen.

6. Account for the fact that a mixture of hydrogen and oxygen *explodes* on ignition, seeing that the volume of the product is *less* than that of the mixture, under the same conditions of temperature and pressure.

7. State the theory of Avogadro and explain its importance for the determination of (a) molecular weights; (b) atomic weights.

8. When two volumes of hydrogen are exploded with one volume of oxygen, two volumes of steam are produced under the same conditions of temperature and pressure. What information does this fact give about the formula for the molecule of oxygen?

9. Give a clear account of the reasons for concluding that the molecular weight of hydrogen is *twice* its atomic weight.

10. Explain the meaning of the following terms, and give two examples to illustrate each:—atomic weight, molecular weight, vapour density, atomic heat, valency, gram-atom, gram-molecule.

11. 2 g. of carbon combine with 5.33 g. of oxygen to form a gaseous oxide. Given the atomic weights of carbon (12) and oxygen (16), calculate the *simplest* formula for this oxide. Its density is 22 ($H = 1$); deduce the true molecular formula.

12. An oxide of carbon contains 42.85 per cent. of carbon. Deduce its *simplest* formula. Also find its molecular formula, supposing its relative density is (a) 14, (b) 42.

13. A certain volatile liquid was found to be composed of 37.5 per cent. carbon, 12.5 per cent. hydrogen, 50 per cent. oxygen. Its vapour density is 16 times that of hydrogen. Find the formula of the substance.

14. A gas contains 85.71 parts of carbon to 14.29 of hydrogen. Its density relative to hydrogen is 14. Calculate (a) its simplest formula, (b) its true formula.

15. Two hydro-carbons, *A* and *B*, have the same percentage composition, viz. 92.3 parts of carbon and 7.7 of hydrogen. The density of *A* is 13, of *B* 39; determine their molecular formulæ.

16. The atomic weight of lead is 206.4 ($O = 16$), and it is found that 13.67 g. of a certain compound contains 12.39 g. of lead and 1.28 g. of oxygen. Find a formula for the compound.

17. 0.1 g. of a metal on solution in dilute acid gave off 34.15 c.c. of hydrogen at S.T.P. Calculate the equivalent of the metal.

18. State the law of Dulong and Petit and point out its importance in the determination of atomic weights.

Explain how the atomic weight of a newly discovered metal would be ascertained.

19. 1 g. of a metal X gave on solution in hydrochloric acid 1242 c.c. of hydrogen measured at normal pressure and temperature. The specific heat of the metal was found to be 0.23. Calculate its equivalent, valency, and atomic weight. What would be the simplest formula for its chloride?

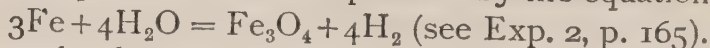
20. Calculate the molecular weights of the following substances:—

(a) Lime, CaO ; (b) turpentine, $\text{C}_{10}\text{H}_{16}$; (c) glycerine, $\text{C}_3\text{H}_8\text{O}_3$; (d) soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; (e) alcohol, $\text{C}_2\text{H}_6\text{O}$; (f) alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

21. Using the atomic weights given on p. 274, calculate the percentage gravimetric composition of the substances in question 20.

22. Find the simplest formulae for compounds having the following percentage composition:—(a) Carbon, 92.3; hydrogen, 7.7. (b) An oxide containing 70.01 per cent. of iron. (c) Potassium, 45.95; nitrogen, 16.45; oxygen, 37.60. (d) Zinc, 22.7; sulphur, 11.15; oxygen, 22.23; water, 43.87.

23. Fully explain all that is expressed by the equation



24. State clearly what the following arrangement of symbols expresses:—



25. Using the equation of question 24, calculate:—

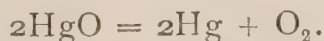
- (a) the weight of zinc sulphate obtainable from 100 g. of zinc and excess of acid;
- (b) the weight of hydrogen obtainable from 20 g. of sulphuric acid and sufficient zinc;
- (c) the weights of (i) zinc sulphate, (ii) hydrogen obtainable when 100 g. of zinc are mixed with 100 g. of sulphuric acid.

26. The equation of the action of heat on potassium chlorate (pp. 104 and 105) is $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$
(potassium chloride)

Calculate the volume of oxygen—

- (a) at S.T.P. obtainable from 2 gram-molecules of the chlorate;
- (b) at 15°C . and 780 mm. pressure obtainable from 100 g. of the chlorate;
- (c) obtainable at 100°C . and 740 mm. pressure when 100 g. of the chloride are simultaneously produced.

27. The action of heat on mercuric oxide (see p. 96) is represented by the equation



Calculate (*a*) the weight of oxide required to yield 10 l. of oxygen at 17°C . and 700 mm. pressure; (*b*) the volume of oxygen at 17°C . and 700 mm. pressure obtainable from 100 g. of the oxide.

28. What volumetric relations can be deduced from the equation $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$?

Calculate the volume of hydrogen at S.T.P. required to combine with 11.2 l. of oxygen (*a*) at S.T.P., (*b*) at 15°C . and 780 mm. pressure, (*c*) at -10°C . and 720 mm.

CHAPTER XVI

THE HALOGENS AND THEIR CHIEF COMPOUNDS

Sources of the halogen elements. The term *halogen* is derived from two Greek words meaning *salt-producer* (*hals*, salt; *gennao*, I produce). Chlorine is the best-known member of the group, and its compound with sodium, viz. sodium chloride or common salt, is the typical salt and, as has already been mentioned, it gives its name to a large class of substances formed by the action of acids on bases. *Chlorine* means *green* (Gk. *chloros*, green), and two other members of the group also have names indicating an obvious property, e.g. *bromine* (Gk. *bromos*, a stench), *iodine* (Gk. *ioeides*, like a violet). The fourth member is *fluorine*, a gas obtained from fluor-spar, a mineral found in Derbyshire, Cumberland, &c.

When sea-water is evaporated, 'bay salt'—a mixture of several chemical salts—is obtained. About two-thirds of this is sodium chloride; traces of sodium bromide and sodium iodide are also found in it, the remainder being chiefly salts of calcium and magnesium.

Sea-weed has the power of absorbing iodides and bromides from sea-water, and originally bromine and iodine were made from *kelp*, the ash of sea-weed. They are now obtained from other sources mentioned later. Sodium chloride occurs in solid beds of *rock-salt** at Northwich in Cheshire and Droitwich in Worcestershire. Occasionally it is found in pure transparent crystals, but more usually in reddish lumps,

* Specimens of rock-salt should be examined in the school museum.

which consist of salt mixed with clay, &c.; the colour is due to traces of oxide of iron. Water flowing over these beds forms a solution of salt known as *brine*, which is pumped up from the wells or mines and evaporated. The greater proportion of the impurities of the rock-salt are insoluble in water, and thus fairly pure salt is obtained.

Revision questions on chlorine and chlorides.

1. What is the shape of a crystal of salt?
2. Do the crystals contain water of crystallization?
3. What is the effect of heat on salt?
4. From what substances have you made salt artificially?
5. What metal does salt contain, and how can it be detected?
6. How can hydrogen chloride be made, using salt?
7. How can hydrochloric acid be made from its elements?
8. Describe the action of hydrogen chloride on (a) litmus, (b) water, (c) sodium hydroxide, (d) zinc, (e) black copper oxide, (f) manganese dioxide.
9. What effect does chlorine produce on moist litmus-paper?
10. Write an equation for the combination of hydrogen and chlorine.

Exp. I. To prepare and examine the properties of a solution of hydrochloric acid.

Required:—As in Figs. 49 and 64; marble, nitre, manganese dioxide, potassium chlorate, tin, litmus, silver nitrate.

Preparation. Fit up apparatus as in Fig. 49,* but attach an inverted funnel as shown in Fig. 64.

Fill one-third of a beaker with water, and arrange the funnel so that it just dips below the surface of the water.

Prepare the gas as in Exp. 49, p. 190,* and make a saturated solution in the beaker.

Properties. Pour some of the solution into test-tubes and examine its action with solutions of litmus, silver nitrate, ammonia.

Note the effects.

Try the action of the acid solution on iron, lead, copper, tin, and marble, warming if necessary. **Note** what happens and test any gas evolved. **Observe** what happens when the acid solution is warmed in test-tubes with oxidizing agents, viz. manganese dioxide, nitre, potassium chlorate.



FIG. 64.

LABORATORY RECORD. Diagrams; tabular list of properties.

Questions:—(i) Why must the funnel (Fig. 64) be only partly covered with water?

(ii) What gases were produced on mixing the acid with iron, tin, and marble? What substances remain in solution?

(iii) What gas is produced when nitre, potassium chlorate, and manganese dioxide are heated, (a) alone, and (b) with hydrochloric acid?

(iv) Write equations for the action of silver nitrate (AgNO_3) on hydrochloric acid and on sodium chloride (NaCl).

PROBLEM (XVI. I). Examine the action of concentrated sulphuric acid on *calcium chloride*, *iron chloride*, and *zinc chloride* in test-tubes.

* i. e. a large flask containing a layer of common salt, placed on a retort-stand and fitted with a right-angled exit-tube and thistle funnel. Concentrated sulphuric acid is poured into the flask.

Exp. 2. To prepare pure chlorine and examine some of its properties.

Required:—As in Fig. 65; commercial hydrochloric acid, manganese dioxide, deflagrating spoon, taper, litmus, Turkey-red twill, hydrogen generator, slaked lime.

Precaution:—*The gas should be made in a draught-chamber, and particular care taken to avoid breathing it.*

Preparation. Fit up apparatus as in Fig. 65; use corks previously boiled in paraffin wax, bend the tubes correctly, and see that there are no leaks.

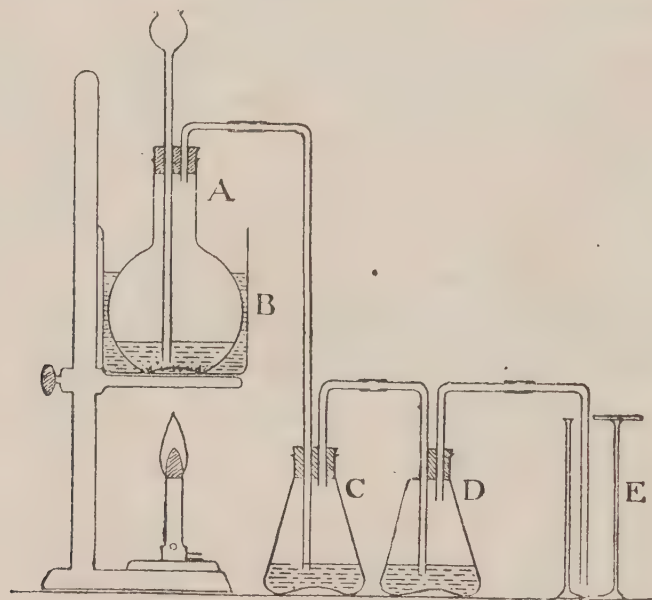


FIG. 65.

Into A slide enough manganese dioxide to make a layer 1 cm. deep. In C place some water, and in D some concentrated sulphuric acid.

Pour commercial hydrochloric acid down the funnel so as to cover the solid well. Place beside you a flask (X) containing some slaked lime.

Heat the water-bath, and collect the gas in jars by downward displacement of air. Place the exit-tube in the flask X when the gas is not being collected.

Properties. (a) Attach a wax taper or candle to a deflagrating

spoon; put the lighted taper into the gas and prevent the products from escaping by means of the metal disk. **Note** the appearance of the flame and the two products of combustion.

(b) Place the following in the gas after moistening them with water:—blue litmus-paper, red twill, a piece of newspaper with some writing-ink upon it. **Note** the effects.

(c) Introduce a piece of *recently dried* red twill and cover with a plate, leave it for some time, and compare the result with that obtained in (b).

(d) Put a *small* piece of dry phosphorus in a clean deflagrating spoon and place it in a jar of the gas. **Note** what happens.

(Be careful to burn off the residual phosphorus in a draught-chamber.)

(e) Pour some water into another jar of chlorine, cover and shake. Invert in a basin of water. **Note** to what extent chlorine dissolves. Slip a plate over the mouth of the jar, remove from the basin, and pour the contents into a flask. Cork up and keep the 'chlorine water' obtained for Problem 3, below.

(f) Shake up the lime in the flask X, and turn out the contents into a basin; **note** its smell.

Put a little of the powder in a test-tube and add a few drops of hydrochloric acid. **Note** the effect and find whether the gas produced bleaches moist litmus-paper. The solid is called *bleaching powder*.

N.B.—Keep the apparatus for Exp. 3.

LABORATORY RECORD. Diagram; full observations of *a*, *b*, *c*, *d*, *e*, and *f*, with an account of minor experiments.

Questions:—(i) What would you expect to happen when a solution of hydrochloric acid is gradually heated till it boils?

(ii) Give reasons for heating the flask in a *water-bath*.

(iii) What is the object of the water in *c* and the sulphuric acid in *D* (Fig. 65)?

(iv) Under what conditions does chlorine bleach?

[Over.

- (v) What substance readily absorbs chlorine, and how may the gas be regained from it?
- (vi) What gases are produced when (a) sulphuric acid acts on salt, (b) hydrochloric acid acts on manganese dioxide?
- (vii) What gas would you expect to obtain by heating a mixture of salt, sulphuric acid, water, and manganese dioxide?

PROBLEMS (XVI. 2). 1. Find whether *sulphur, charcoal*, a filter-paper moistened with *turpentine*, burn in chlorine.

2. Test the correctness of your answer to question vii. Use a mixture of equal volumes of acid and water.

3. Half fill an inverted flask with chlorine by displacement of water. Expose it to sunlight for some days, the flask remaining inverted in a basin of water. Observe it from time to time, and discover what has been formed when the colour has disappeared.

Exp. 3. To prepare chlorine from salt and to examine its action on some metals.

Required:—As in Figs. 65 and 66; salt, manganese dioxide, sulphuric acid, measuring jar, mortar, beaker, slaked lime, copper wire, sodium, iron filings, mercury, silver nitrate, grease, gas-jars.

Preparation. Use the apparatus as in Fig. 65. Place 40 c.c. of water in a beaker, carefully add 50 c.c. of concentrated sulphuric acid from a measuring jar. Stir the mixture and cool it. Mix about 25 g. of salt with 18 g. of manganese dioxide in a mortar, and put it into the flask A. Fix the connexions, see that they are air-tight, pour in some of the diluted acid, and heat the water-bath. Fill three jars with the gas, cover with greased plates, and put the exit-tube in a flask containing slaked lime to prevent chlorine from escaping into the air.

Action on metals. (a) **Copper**. Roll a piece of copper wire into a spiral and attach it to a deflagrating spoon. Heat the wire and plunge it into a jar of chlorine. **Note** the result, and when the jar is cold, pour in water. Identify the product in solution.

(b) **Iron.** Place a few pieces of clean iron wire in a small straight hard-glass tube open at both ends, as in Fig. 66. Pass chlorine through the tube and heat the iron. **Note** the character of the substance produced.

When cold, shake the contents into a basin and add water.

Stir and divide the clear liquid into two portions; to one add silver nitrate, to the other add sodium hydroxide, and try to identify the solid, which is a product of double decomposition.

(c) **Sodium.** Place a small piece of clean sodium in a bulb-tube as shown in Fig. 66, and pass chlorine over it. Heat gently, and if no action takes place, quickly slip a roll of moist filter-paper into the bulb-tube at *T*. Connect up again and **note** whether there is any action. Continue to pass chlorine, and heat the sodium until the latter is all changed.

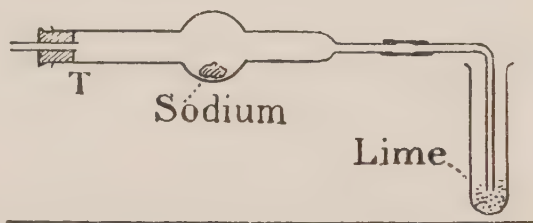


FIG. 66.

When all is cold, disconnect and carefully pour water through the bulb-tube, collecting the liquid in a basin. Test the substance in solution for sodium and for a chloride.

(d) **Mercury.** Put a drop of mercury into a bulb-tube and pass chlorine over it. Heat *gently* and **note** the result. Avoid breathing the fumes.

N.B.—Keep the generator for Exp. 4.

LABORATORY RECORD. List of observations. Name the products.

Questions:—(i) Is the presence of water necessary in order that any of these actions may take place? Mention any other chemical actions which are accelerated by the presence of water.

(ii) By what other reaction has anhydrous cupric chloride been produced? Write an equation for it and for (a).

(iii) Write equations for the formation of sodium and mercuric chlorides, given that Na and Hg represent atoms of the metals, and that their valencies are 1 and 2 respectively.

Exp. 4. To show the oxidizing power of moist chlorine.

Required:—Saturated chlorine water, yellow lead oxide, small flask, filter, porcelain basin, ignition tube.

DIRECTIONS. Put about 5 grams of yellow lead oxide in a flask and add a large test-tubeful of chlorine water. Set the flask on gauze, heat gently and shake.

Now heat nearly to boiling and add chlorine water until *all* the solid has a chocolate colour.

Boil till all chlorine has escaped, and collect the solid (*X*) on a filter-paper and the liquid in a basin.

Wash the solid on the filter-paper with hot water and set the paper to dry in an air-oven at 110°C .

Test the clear liquid with litmus, then evaporate and try to identify the solid (*Y*) obtained.

Scrape a little of the dry solid (*X*) from the filter-paper into an ignition tube; heat strongly and test for oxygen.

Note the character of the residue.

Heat a little of *X* with hydrochloric acid and test any gas evolved with moist litmus-paper.

LABORATORY RECORD. Description and observations.

Questions:—(i) Does the solid *X* contain a greater proportion of oxygen than yellow lead oxide? Quote evidence for your answer.

(ii) What solid should result from the action of hydrochloric acid on yellow lead oxide (a basic oxide)?

(iii) If the chlorine takes hydrogen from water, what becomes of the oxygen and hydrochloric acid which would be formed?

(iv) What is the composition of *Y*? Explain how it came to be formed. What is the composition of *X*?

Exp. 5. The action of chlorine on caustic potash.

Required:—As in Fig. 65; caustic potash, evaporating basin, potassium chlorate, silver nitrate.

DIRECTIONS. Use the chlorine generator of Exp. 2 (p. 290), and put a cold weak solution of caustic potash into c (instead of water) and a strong solution into d (instead of sulphuric acid). The potash solutions should be about 2 cm. deep. Pass the gas through till no more seems to be dissolved in either flask. To a little of the liquid from c add a few drops of hydrochloric acid; **note** what happens and compare the result with that in Exp. 2 (f).

Transfer half of the contents of d to an evaporating basin and boil for some time in a draught-chamber. Allow it to cool when crystals *begin* to form. Collect the first crop of crystals, wash in a *little* pure water, and dry them.

Heat a small portion in an ignition tube and test the gas evolved with a glowing splinter. These are crystals of *potassium chlorate*, but may be mixed with a little potassium *chloride*, which is formed simultaneously. The former is less soluble than the latter, and crystallizes out first, unless the evaporation has been carried too far.

Take a crystal of *pure* potassium chlorate from a bottle, dissolve it in *pure* water, and add a few drops of silver nitrate solution. Heat another crystal in an ignition tube until some oxygen has come off. Dissolve the residue in pure water, add silver nitrate, and **note** the effect.

LABORATORY RECORD. Brief description; complete observations.
Questions:—(i) Compare the action of a cold dilute solution of caustic potash on chlorine with that of slaked lime.

(ii) What substances are formed if the alkalis are hot?

(iii) By what two tests may potassium chlorate be distinguished from potassium chloride?

(iv) What two products are formed when potassium chlorate is heated?

Electrolysis of hydrochloric acid. If a *strong* solution of the gas is decomposed by an electric current, hydrogen and chlorine are produced and may be collected separately. It is necessary to use electrodes of gas-carbon, since chlorine combines with platinum. As chlorine is much more soluble in water than hydrogen, the gases should not be collected until the liquid is saturated with chlorine. Then the ratio between the volumes can be ascertained approximately.

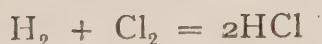
Bleaching powder and its uses. Exp. 2 (*f*) showed that chlorine is readily absorbed by dry slaked lime. The product is known as 'bleaching powder' or 'chloride of lime'. It is, however, quite distinct from calcium chloride. The use of chlorine as a bleaching agent would be limited if it were not possible to absorb it in a solid in this way, since a gas is awkward and expensive to transport. By the addition of any dilute mineral acid (hydrochloric works best) the chlorine is liberated from the powder. It is used very largely for bleaching *vegetable* colouring matters, more especially calico and paper. It will not bleach mineral colours or printer's ink.

Pure chlorine will not bleach when dry, but does so if moisture is present. Hydrochloric acid is always formed as a product of the action, which is supposed to consist in (*a*) the decomposition of water by the chlorine, with formation of hydrochloric acid and oxygen (an action known to go on when 'chlorine water', i.e. a solution of chlorine in water, is exposed to sunlight as in Prob. 3, p. 292); (*b*) the union of the 'nascent' oxygen with the colouring matter, which becomes oxidized to a colourless compound.

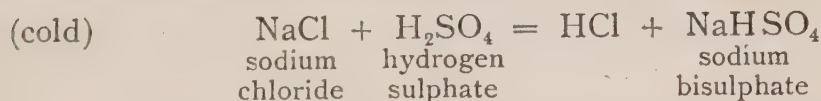
The material to be bleached is first 'soured' by being dipped into a solution of hydrochloric acid; then it is passed into a mixture of bleaching powder and water. Chlorine is evolved and the colouring matter is bleached. The material is then rinsed in water to get rid of the acid and traces of the powder.

Equations for the reactions of chlorine and chlorides.
On p. 271 evidence was given showing that the symbol HCl represents a molecule of hydrogen chloride. The necessary evidence leading to the establishment of the formulae for the other substances involved in these reactions would take too long to explain in detail, and will therefore be assumed.

Preparation of hydrogen chloride. (1) Synthesis, i.e. burning hydrogen in chlorine (p. 210) and action of light on the mixed gases (p. 238).



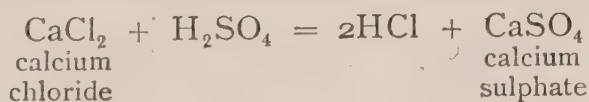
(2) Action of concentrated sulphuric acid on a metallic chloride (p. 188). With common salt there are two stages:—



The whole reaction may be expressed in a single equation, by omitting the intermediate product, NaHSO₄:—



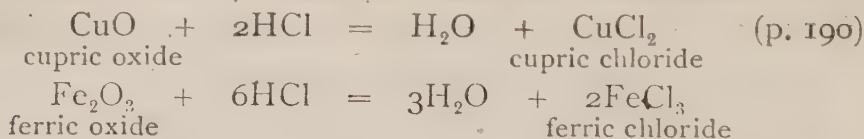
Other metallic chlorides act in a similar manner, e. g. :—



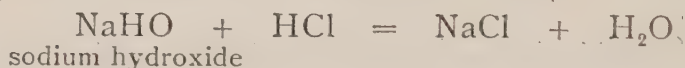
Reactions of hydrogen chloride. (1) With *metals*. Most metals react quickly, yielding hydrogen and a metallic chloride, e. g. magnesium, zinc, iron, tin, aluminium, sodium, &c. Some have either a very slow action or none at all, e. g. lead, copper.



(2) With *basic oxides*, a salt and water are formed.



(3) With *metallic hydroxides*, a salt and water are formed (p. 189).

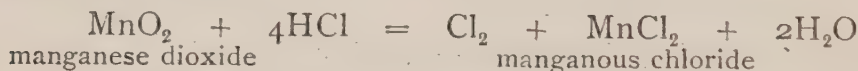


(4) With *carbonates*, carbon dioxide, a salt, and water form.



Marble is a natural form of calcium carbonate.

Preparation of chlorine. (1) By the action of a peroxide or other highly oxidized substance on hydrogen chloride (pp. 200 and 290).

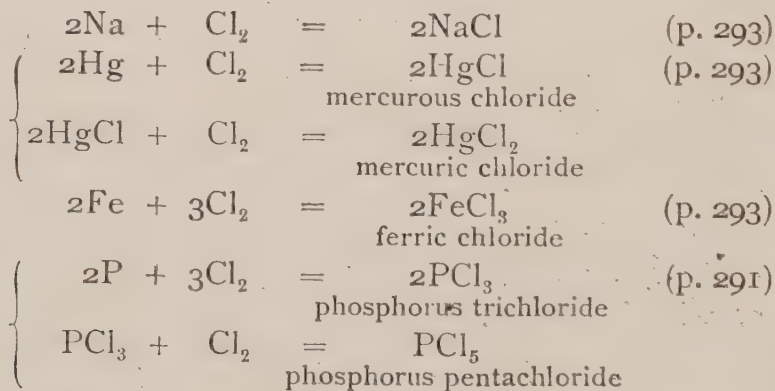


Note that only half the chlorine of the acid is obtained as free chlorine.

(2) From salt (p. 292).



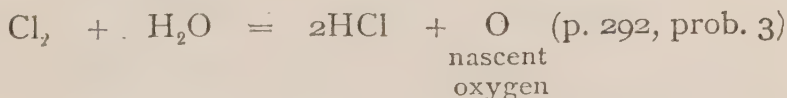
Reactions of chlorine. (1) Syntheses with *metals and non-metals*.



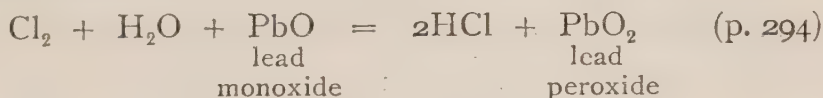
(2) With *hydro-carbons* when heated, e.g. candle, turpentine, &c. (pp. 290-3).



(3) With *water*, oxygen is produced, hence moist chlorine is a powerful oxidizing agent.



If any oxidizable substance is present, the nascent oxygen reacts with it, e. g. :—

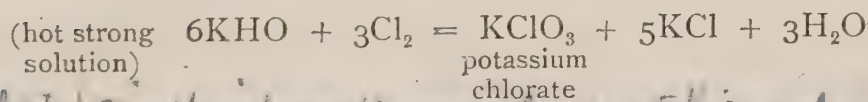
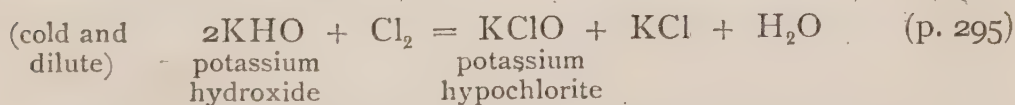


[A secondary action between excess of the monoxide and the acid occurs also, viz. :—



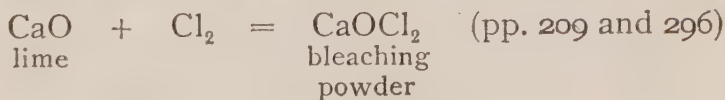
Litmus and vegetable colouring matters are bleached owing to the action of nascent oxygen on them. The oxidized colouring matter is white.

(4) With *alkalis*, in cold dilute solutions, hypochlorites and chlorides are formed; but on heating, or in hot strong solutions, the hypochlorite yields a chlorate and a chloride.

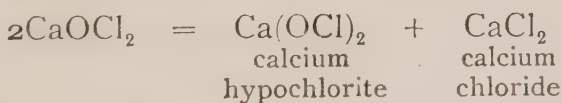


the chlorate being sparingly soluble readily crystallizes out. Filter & recrystallize from a small amount of hot water.

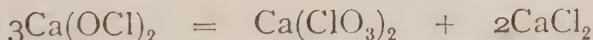
Sodium hydroxide reacts in a similar manner.



On treating bleaching powder with water calcium hypochlorite and calcium chloride are formed.



On heating the hypochlorite solution, calcium chlorate is formed.



Potassium chlorate is obtained on a large scale by passing chlorine into hot milk of lime. This produces calcium chlorate in solution. Add to this a strong solution of KOH & on concentrating crystals of KClO₃ are obtained.

On adding a solution of potassium chloride to this solution, potassium chlorate is formed.

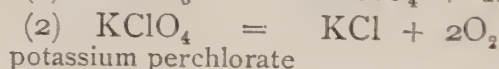


This is the method for the preparation of potassium chlorate on the large scale; it is less soluble than calcium chloride, and separates out first on crystallizing.

Hypochlorites are distinguished from chlorates, chlorides, &c., by the fact that they yield chlorine when treated with a *cold* diluted mineral acid.



The action of heat on potassium chlorate proceeds in two stages:—



potassium perchlorate

The perchlorate decomposes at a higher temperature than the chlorate, and if the heating is stopped at stage 1 the perchlorate may be obtained by fractional crystallization.

The chemical activity of chlorine. The foregoing experiments show that chlorine reacts with a large number of elements and compounds. It is even a more active substance than oxygen, combining with nearly every element at comparatively low temperatures.

As a *supporter of combustion* it is more energetic than oxygen, as a lower initial temperature is required for combination. Compounds of carbon, however, burn more feebly than in oxygen; the hydrogen they contain combines to form hydrochloric acid, and free carbon is deposited, as is evident from the smoky nature of the flame. Carbon is one of the few elements which does not combine *directly* with chlorine.

Handwritten notes:
 HClO_3 is also obtained by the electrolysis of HCl and
 Potassium is set free at the cathode & chlorine at the anode.
 The Potassium acts on the water to form KOH & H_2 .
 $2\text{H} + 2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$ & when the chlorine & ammonia
 bottles are brought into contact, HCl & NH_3 is produced.

Exp. 6. The action of sulphuric acid on potassium bromide and iodide.

Required:—As above, test-tubes and stand, litmus-paper, manganese dioxide.

DIRECTIONS. *A.* Put a small quantity of each solid in a separate test-tube and add about 5 c.c. of concentrated sulphuric acid. **Note** any action, let the tubes stand in a draught-chamber, test the fuming gases with moist neutral litmus-paper.

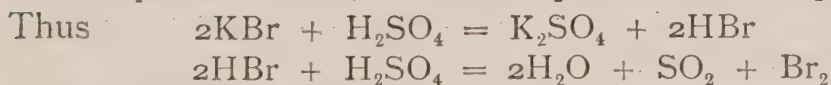
B. Repeat *A*, using diluted acid (1:4); gently heat each tube. Add a little powdered manganese dioxide to each and continue to warm the tubes in the draught-chamber.

LABORATORY RECORD. Observations, noting similarities and differences in the behaviour of the two salts.

Questions:—(i) Was an acid produced in each case? If so, was any other product formed at the same time? Would the action be a suitable means of making the acids?

(ii) Account for the actions of manganese dioxide in *B*. Write equations assuming KBr and KI are the molecular formulae of the salts, and that the action is similar to that of common salt on these reagents.

Preparation of bromine and iodine. Hydrogen bromide and iodide are formed in Exp. 6 *A*, in small quantities, but owing to their instability in presence of oxidizing substances (in this case sulphuric acid) they are quickly decomposed, giving bromine and iodine respectively, together with water and sulphur dioxide, reduction products of sulphuric acid.



The usual method is to heat a mixture of potassium bromide or iodide with manganese dioxide and diluted sulphuric acid in a retort, when the halogens will pass over with the steam and are condensed in the receiver.

Representing the halogen element by Ha, the action is shown by the equation:—



Exp. 7. To prepare bromine and iodine and to examine their properties.

Required:—As in Exp. 6 and Fig. 67; 150 c.c. flask, carbon bisulphide, benzene, starch, iron filings, mercury, sulphur, fresh sulphurous acid, sodium thiosulphate.

Precaution:—*Avoid inhaling the poisonous vapour of bromine. Set up the apparatus in a draught-chamber.*

A. Bromine. Put about 5 g. of potassium bromide and an equal bulk of manganese dioxide powder into the retort, and fill a third of the bulb with diluted sulphuric acid (1:4). Arrange the apparatus as in Fig. 67,*

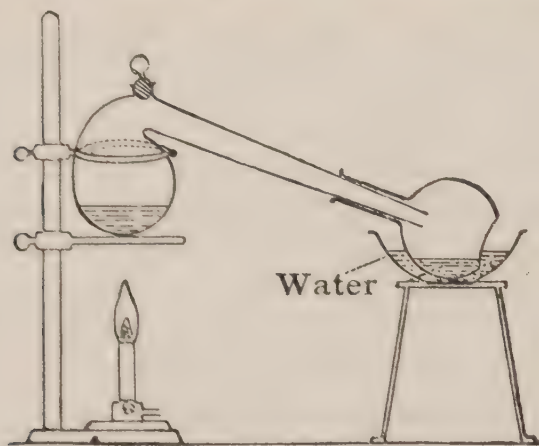


FIG. 67.

and continue to heat gently until orange vapour ceases to escape. Add a little more acid to ensure that the reaction is complete. When no more bromine vapour comes off, remove the receiver and close the mouth with a vaselined cork.

B. Iodine. Repeat *A*, using the iodide instead of bromide of potassium, and continue until the purple vapour of iodine no longer fills the retort. Remove the flame and pour away the contents of the retort. Having loosened the solid iodine from the neck of the retort

* Or the receiver may rest on a ring under a water-tap.

by means of a glass rod, wash it down into the receiver with water.

Properties. C. Examine solubility (1) in water, by adding distilled water to the two receivers and shaking vigorously; (2) in carbon bisulphide; (3) in benzene, by shaking up a little of the liquid from (1) in test-tubes with carbon bisulphide and benzene. **Note** results. N.B.—*Keep all flames away from the liquids.*

D. Examine the action of iodine with potassium iodide solution. Repeat, using bromine water instead of iodine, and find out whether iodine is now in solution.

E. Boil some water in a small basin and, having made a creamy mixture of a little starch with cold water, pour the latter into the basin of hot water. Allow this opalescent liquid to cool. Fill two gas-jars with water and add some cold starch liquid. Now add a solution of bromine to one, and of iodine to the other gas-jar, and **record** the result.

F. Try whether (a) iron filings, (b) mercury, combine with iodine by adding a solution of iodine to small quantities of these metals in test-tubes. Repeat, using bromine.

G. *Oxidizing power of bromine and iodine.* Find out whether (a) bromine water, (b) iodine, can oxidize *sulphur* to sulphuric acid in the presence of water. Test separate portions for a sulphate and for the halogen hydride, in the latter case using silver nitrate. Silver bromide is a very pale yellow, and silver iodide is a darker yellow colour, and both are insoluble in water or acids. Examine the action of bromine and iodine on a freshly made solution of *sulphurous acid*, and determine the nature of the change which has taken place by suitable tests.

LABORATORY RECORD. Diagram; list of comparative properties of the two elements arranged in parallel columns.

[Over.]

- Questions:—*(i) What are the best solvents for (a) iodine, (b) bromine? Does either dissolve in a solution of potassium iodide?
- (ii) What reaction forms a convenient test for traces of free iodine?
- (iii) Write an equation for the action of bromine on sulphurous acid.
- (iv) Does bromine displace iodine from an iodide?
- (v) How is a solution of (a) a bromide, (b) an iodide, distinguished from a solution of a chloride?

Exp. 8. To show the action of chlorine and bromine on potassium iodide and of chlorine on potassium bromide.

Required:—Solutions of chlorine, bromine, potassium bromide, and potassium iodide; carbon bisulphide.

DIRECTIONS. *A.* Add to solutions of potassium iodide in two test-tubes (*a*) chlorine water, (*b*) bromine water. Add a few drops of carbon bisulphide and shake.

N.B.—*Carbon bisulphide is very inflammable.*

B. Add chlorine water to a solution of potassium bromide, and determine by the addition of carbon bisulphide and shaking whether bromine has been set free.

LABORATORY RECORD. Observations in *A* and *B*.

Questions:—(i) What other tests for bromine and iodine might be used instead of solution in carbon bisulphide?

(ii) Supposing that excess of chlorine and bromine were added in *A* and of chlorine in *B*, what substances would be left in solution? Write equations for these reactions.

The oxidizing power of the halogens is shown by their action on sulphur and sulphurous acid. The halogen takes the hydrogen from the water present and leaves the oxygen free to combine with the reducing agent.



The smaller the energy with which the halogen combines with hydrogen, the weaker will be its oxidizing power, so that chlorine is the strongest and iodine the weakest oxidizing agent of these three halogens.

The same thing is shown by the action of sulphuric acid on the haloid salts, and by the action of the halogens on salts of the other two. The most electro-negative element is chlorine, and the least electro-negative, iodine, which therefore has the smallest attraction for the strongly positive metals sodium and potassium, and is therefore expelled from combination with them both by bromine and chlorine.

Preparation of hydrogen bromide and iodide. The ready oxidation of these acids prevents their preparation by the action of sulphuric acid on the haloid salts. The usual method is to act on phosphorus bromide or iodide with water. In the first case, bromine is added by means of a tap funnel to a mixture of red phosphorus and water, but in the case of hydrogen iodide, water is added to a mixture of iodine with red phosphorus. In order to remove traces of halogen carried over with the halogen hydride, the gas is passed through a U-tube containing some red phosphorus.

Exp. 9. To prepare hydrogen iodide.

Required:—As in Fig. 68; red phosphorus, iodine, beaker.

DIRECTIONS. Weigh out into a beaker, placed on the pan of a rough balance, 30 g. of iodine, and into another beaker 5 g. of dry red phosphorus. Transfer both substances to a dry flask, and having set up the apparatus as in Fig. 68, pour 5 c.c. of water into the tap funnel.

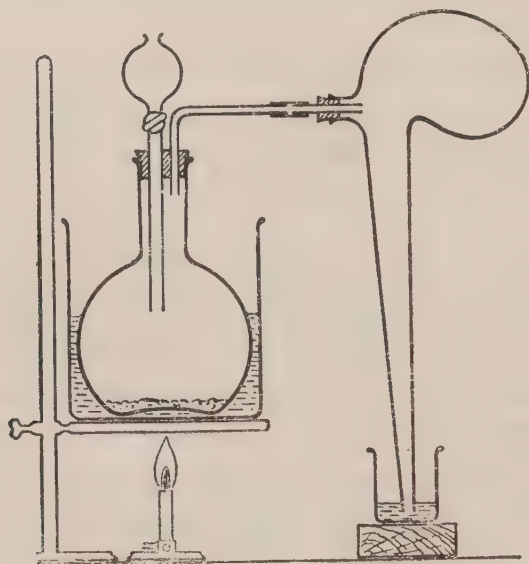


FIG. 68.

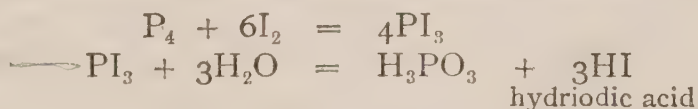
Heat the water-bath nearly to boiling and run water from the funnel into the flask a few drops at a time. The hydrogen iodide will be formed and will pass out into the retort. **Note**

results, and as soon as action ceases after addition of more water, disconnect the retort and allow the water to run from the retort into the beaker. Transfer the liquid, which is a solution of hydrogen iodide, to a corked flask.

Examination of solution A. Test different portions in test-tubes with (1) litmus-papers; (2) silver nitrate solution; (3) sulphuric acid, heating gently; (4) manganese dioxide, heating gently. **Note** results.

The substances left in the generating flask are a solution of phosphorous acid and excess of phosphorus.

When chlorine, bromine, or iodine are mixed with red phosphorus, phosphorus chloride, bromide, or iodide are formed, and the addition of water to any of these gives the halogen hydride and phosphorous acid. Thus,



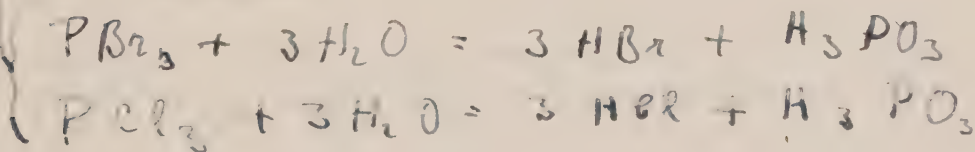
LABORATORY RECORD. Diagram; description of the preparation; list of observed properties of hydriodic acid.

Questions :—(i) Is hydrogen iodide very soluble or only moderately soluble in water?

(ii) Why was a retort used in Fig. 68?

(iii) Is hydrogen iodide an acid?

(iv) Make a list of the chief properties of the (a) chloride, (b) iodide of hydrogen, to show their similarities and dissimilarities.



Properties of the halogen hydrides. The halogen hydrides are all fuming gases very soluble in water, giving strongly acid solutions. They are all monobasic (i. e. 1 molecule contains 1 atom of replaceable hydrogen), and their salts are very similar. All are soluble in water except the mercurous and silver salts; but those of lead, though only slightly soluble in cold, dissolve fairly easily in hot water.

Whilst the combination of chlorine with hydrogen is easily and completely brought about under the influence of heat, light, or electric discharge, this is not the case with bromine and iodine.

Bromine vapour supports the combustion of hydrogen, partial combination taking place, which is rendered complete by passage of the mixed gases through a hot tube or a catalytic accelerator, such as finely divided platinum.

Hydrogen and iodine vapour only partially combine when passed through a hot tube, but combination is not rendered complete by the presence of platinum.

There is, in fact, a gradually decreasing stability in passing from hydrogen chloride to hydrogen iodide, which is closely connected with the heats of formation of these substances.

By burning hydrogen in chlorine in a suitable calorimeter and determining (a) the rise in temperature of the calorimeter, (b) the weight of hydrogen chloride formed, the heat evolved during the formation of 1 gram-molecule can be calculated. This is called the 'heat of formation' of hydrogen chloride, and amounts to 22,000 calories.

Indirect methods show that a gram-molecule of hydrogen bromide gives out 12,100 calories, but a gram-molecule of hydrogen iodide *absorbs* 6,100 calories in its formation.

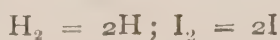
Hydrogen chloride and hydrogen bromide are said to be *exothermic* substances, whilst hydrogen iodide is *endothermic*. An endothermic substance can only be formed if heat or some other form of energy is supplied from external sources.

Although the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ only takes place to a small degree even under the influence of heat, the elements may be caused to combine if a reaction is proceeding simultaneously which gives out heat.

Thus $\text{H}_2\text{S} + \text{I}_2 \rightarrow 2\text{HI} + \text{S}$ does not take place unless water is present. The minute trace of HI first formed reacts with the water, giving out much

heat; this heat enables more iodine to react with hydrogen sulphide, and the reaction only ceases when the solution of HI has become sufficiently concentrated for the heat evolved by addition of more HI to become negligible.

We must suppose that the heat of formation is negative, because the heat absorbed by the reactions



is greater than the heat evolved by



Fluorine. In Derbyshire and other limestone localities a mineral called *fluor-spar* is found in cubic crystals. It has long been used in extracting certain metals, for, on account of its low melting-point, it forms a fluid or flux which helps in the separation of the metal from the rest of the ore.

The Swedish chemist Scheele showed that on treatment with sulphuric acid a fuming gas, very like hydrochloric acid, was formed. This is called hydrofluoric acid, and was proved to contain hydrogen and another element which, owing to its great chemical activity, could not be isolated. This element is fluorine, and was not obtained in the free state until 1886, when the French chemist Moissan succeeded in electrolysing the acid and in collecting gaseous fluorine.

This pale yellow gas has a density of 19, its molecular weight is 38, and atomic weight 19. F_2 represents its molecule. It is one of the most active chemicals known, exceeding the activity of chlorine. It combines with hydrogen explosively even in the dark, forming hydrogen fluoride (HF). It decomposes water, combining with the hydrogen and liberating oxygen in the form of ozone (O_3); it supports the combustion of a very large number of substances, combining directly with nearly all the elements, oxygen being an exception. It attacks glass, forming silicon fluoride (SiF_4), and it liberates chlorine from chlorides, bromine from bromides, and iodine from iodides. There are, in fact, very few substances with which it does not react.

Exp. 10. To obtain hydrogen fluoride and to examine its properties.

Required:—Lead basin, calcium fluoride, glass plate, paraffin wax, sulphuric acid, solutions of hydrofluoric acid, calcium chloride, silver nitrate.

Precaution:—*Perform this experiment in a fume-cupboard; on no account must hydrogen fluoride be inhaled.*

DIRECTIONS. *A.* Cover the bottom of the leaden bowl with a thin layer of calcium fluoride and place it on a tripod. Heat a glass plate hot enough to melt some wax placed on it, and rub with a rag until an even coating has formed. Cool, and cut a design through the wax with a sharp-pointed instrument.

Pour a few c.c. of sulphuric acid into the lead bowl, place the glass, waxed side downwards, on the top, warm gently, remove the flame, and leave for 5 minutes. Remove the plate and pour water into the bowl. Warm the plate and remove the wax with a rag. **Note** the appearance of the glass plate. Glass instruments, e.g. eudiometers, burettes, thermometers, &c., are etched by painting them with a solution of this gas, the rest being covered with wax.

B. Pour a few drops of diluted hydrofluoric acid into two beakers half filled with distilled water. Test the solution in one with litmus-papers, and then add a few drops of calcium chloride and a drop of ammonia solution; to the other add a solution of silver nitrate.

Note any changes which take place.

Owing to the action which hydrogen fluoride has upon glass, vessels of lead are used in the preparation of its solution from fluor-spar and sulphuric acid on a larger scale.

LABORATORY RECORD. Observations in *A* and *B*.

- Questions*:—(i) Glass may be regarded as a compound of SiO_2 with certain metallic oxides. If SiF_4 is formed (a gas), what other products are likely to be formed by the action of hydrogen fluoride (HF) on glass?
- (ii) Write an equation for the action of sulphuric acid on fluor-spar (CaF_2).
- (iii) Which gives the more strongly acid solution, hydrogen chloride or hydrogen fluoride?
- (iv) Compare the action of soluble silver and calcium salts with hydrochloric and hydrofluoric acids.

Pure hydrogen fluoride. The usual method of preparing this very dangerous gas is to heat the solid compound which it forms with potassium fluoride. This substance is placed in a platinum retort connected with a platinum U-tube placed in a freezing mixture. Hydrogen fluoride comes off and is condensed to a liquid in the U-tube.

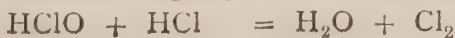
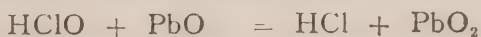


At atmospheric pressure hydrogen fluoride boils at 19.5°C ., the boiling-points of the other halogen hydrides being very much lower than this.

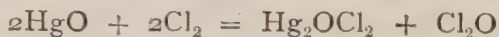
It was shown by Thorpe that the vapour density of the gas near its liquefying point corresponds to a formula H_2F_2 . This fact accounts for its high boiling-point, since as a rule greater complexity in the molecule is associated with higher boiling-point. We can also understand the existence of salts such as KHF_2 , the acid in reality being dibasic.

The oxides and oxyacids of the halogens. When chlorine, bromine, or iodine is passed into a solution of potassium hydroxide, a mixture of salts is formed, and if the atom of the halogen is represented by Ha , they consist of KHaO and KHa . When the solution of the mixture of salts is boiled, a part of the oxysalt undergoes oxidation at the expense of the rest. Thus, $3\text{KHaO} = \text{KHaO}_3 + 2\text{KHa}$. Such a change as this is called self-oxidation, and takes place owing to the instability of the salt of the type KHaO . The acids of the type HHaO are even more unstable than their salts, HIO , hypoiodous acid least stable, hypobromous acid, HBrO , next, and HClO acid the most stable of the three.

Hypochlorous acid can only be obtained in dilute solution. It very readily parts with oxygen, and is a very powerful oxidizing agent.



Chlorine monoxide. By passing chlorine over cold dry yellow mercuric oxide a reddish-yellow gas, chlorine monoxide, Cl_2O , is formed.



It is an explosive substance, and when dissolved in water gives HClO . It is therefore an acid anhydride.

Chlorine dioxide. When sulphuric acid is mixed with potassium chlorate, a dark red solution is formed which evolves a yellow gas, chlorine dioxide, ClO_2 .

Like Cl_2O it is unstable and explodes on warming. It is not the anhydride of an acid.

Fluorine and bromine have no oxides. Iodine has a fairly stable solid oxide, I_2O_5 .

Perchlorates. By heating potassium chlorate carefully, oxygen is evolved, and a mixture of potassium perchlorate, KClO_4 , with potassium chloride is formed. It is only slightly soluble in water, and can therefore be readily obtained free from chloride by recrystallization.

When heated it decomposes.



QUESTIONS ON CHAPTER XVI.

Give equations whenever possible.

[Assume that 1 gram-molecule of a gas occupies 22.4 l. at S.T.P.]

1. How do you account for the presence of salt in sea-water? How is salt obtained on the large scale?
2. Describe the preparation of hydrochloric acid, using salt. How is the gas collected? How can a solution be made?
3. Enumerate the chief physical properties of hydrochloric acid; describe its action with zinc, iron, tin, lime, marble, copper oxide.
4. How do oxidizing agents react when heated with hydrochloric acid?
5. How can you prove that hydrochloric acid contains (a) hydrogen, (b) chlorine?
6. How is chlorine gas most conveniently made from hydrogen chloride? What impurities is it liable to contain, and how can it be separated from them? Describe its action on water.
7. Describe the conditions under which chlorine bleaches. How is bleaching powder made, and how is it used in bleaching?
8. Give an account of experiments to show that chlorine will support the

combustion of (a) a non-metal, (b) a metal, (c) a compound. Name the products in each case.

9. What action has chlorine on iron, lead, tin, mercury, copper, and sodium? Describe the conditions of the action and the obvious properties of the products.

10. Contrast the action of oxygen on metals, non-metals, and hydrocarbons with that of chlorine.

11. Explain in detail how pure chlorine can be obtained directly from common salt.

12. Explain fully how the volumetric composition of hydrochloric acid gas can be ascertained by synthesis, and how its molecular formula can be deduced.

13. Describe an experiment to show the oxidizing power of moist chlorine.

14. What is the action of chlorine on (a) a cold dilute solution of potassium hydroxide, (b) a strong hot solution?

What substances result from boiling bleaching powder and water? How would you proceed in order to obtain potassium chlorate from the hot mixture?

By what tests could you distinguish between the (a) chloride, (b) hypochlorite, (c) chlorate of potassium?

15. Compare the properties of (a) a *mixture* of equal volumes of hydrogen and chlorine with those of (b) the *compound* hydrogen chloride gas. Consider the obvious properties and action of water, litmus, lighted taper, metals, oxides, marble, &c.

16. Chlorine was formerly supposed to be an oxide of an unknown element. Give as complete reasons as possible for concluding that it is an element.

17. Calculate the weights of salt required to yield the following quantities of hydrochloric acid (a) 100 g., (b) 20 l. at S.T.P., (c) 20 l. at 17° C. and 740 mm. pressure.

18. What weight of chlorine is obtainable from 150 g. of hydrochloric acid by warming it with manganese dioxide? What volume will the gas occupy (b) at S.T.P., (c) at 27° C. and 780 mm. pressure?

19. What volume of chlorine at 17° C. and 750 mm. pressure will combine with 10 litres of hydrogen (a) at the same temperature and pressure, (b) at S.T.P.?

20. How many litres of chlorine are required for the combustion of (a) 10 litres, (b) 10 grams of marsh gas (CH_4), the temperature and pressure being normal?

21. Describe the action of sulphuric acid on the chloride, bromide, and iodide of sodium.

22. How are the iodide and bromide of hydrogen prepared? Compare their properties with those of hydrogen chloride, in tabular form.

23. Give an account of the preparation of bromine and iodine from bromides and iodides. Draw up a table to show the similarities and differences in their properties.

24. What is the chief source of fluorine? How can hydrogen fluoride be obtained from it, and how has the element fluorine been isolated?

25. State how glass may be etched by hydrogen fluoride, and explain the chemical change which occurs.

26. Draw up a table of the comparative properties of the four halogen elements.

CHAPTER XVII

THE PERIODIC SYSTEM

SINCE Chemistry first became a science, much work has been done on the study of the classification of the elements into groups, and many attempts have been made to discover some relation between the atomic weights and properties of elements.

That matter is all of one kind, and that the various elements are built up from this primordial substance by some process of condensation, was first suggested by Prout in the year 1815. He thought that hydrogen was this primordial substance, and based his hypothesis on the supposition that the atomic weights of all elements were whole numbers, that of hydrogen being taken as unity. The hypothesis gave a great impetus to the determination of atomic weights, but the Belgian chemist Stas, whose work in this department attained a degree of accuracy hitherto unknown, proved that the hypothesis was without experimental foundation.

The fact that in a triad of elements so closely related in chemical properties as to form a family or group, the arithmetical mean of the highest and lowest is approximately the atomic weight of the third element, was first pointed out by Dobereiner, and such groups of elements are known as Dobereiner's triads.

This is well illustrated in the case of the halogens, the atomic weights of these elements being—Cl, 35.5; Br, 80; and I, 127. Now $\frac{35.5 + 127}{2} = 81.75 = \text{A.W. of Br (approx.)}$.

In the case of these elements it was noticed that both the physical and chemical properties vary with the atomic weights,

the non-metallic character becoming less marked as the atomic weight increases. This is particularly well shown in the case of the hydrides, the formation of which by any element is a distinctly non-metallic characteristic. As the atomic weight of the halogen increases, the stability and heat of formation of the hydride decreases.

The heats of formation of the four hydrides are as follows :

HF 38,000 cal. ; HCl 22,000 cal. ; HBr 12,100 cal. ; HI -6100 cal.

A gradation in properties is shown by other compounds of these elements, such as the solubility in water of the salts of the above-mentioned acids with a particular metal, a relationship which is best shown by plotting a curve, as may be done by using the table of solubilities on p. 458.

A similar relation between atomic weight and properties is found to hold in other groups. In 1864 Newlands showed that if the elements are arranged in the order of their atomic weights, the properties of the first element resemble those of the eighth, but with modifications, the eighth element differing from the first just as the octave of a given musical note differs from the note itself.

He called his scheme the *Law of Octaves*. Later, in the years 1870 and 1871, a more satisfactory scheme of classification of the elements was proposed by Lothar Meyer and by the great Russian chemist Mendeléef, the method of arrangement being similar to that of Newlands. Mendeléef called his arrangement the Periodic System, and stated as a general law—**The Periodic Law—that the properties of the elements are a periodic function of their atomic weights.**

The elements are arranged in twelve horizontal series and nine vertical columns or groups. The only element occurring in the first series is hydrogen (see table on opposite page).

The first group, numbered 0, contains the rare gases found in the air, so that the second series begins with helium, which, like the other members of Group 0, is not known to combine with any other element, and has no valency. This

THE PERIODIC SYSTEM

Groups	O	I	II	III	IV	V	VI	VII	VIII
Sub-groups									
Series I		H, 1							
Series 2	He, 4	Li, 7	Be, 9						
Series 3	Ne, 20	Na, 23	Mg, 24	B, 11	C, 12	N, 14	O, 16	F, 19	
Series 4	A, 39.9	K, 39	Ca, 40	Al, 27	Si, 28.4	P, 31	S, 32	Cl, 35.5	
Series 5		Cu, 63.6	Zn, 65.4	Sc, 44.	Ti, 48	V, 51	Cr, 52	Mn, 55	Fe, 56 Co, 59 Ni, 58.7
Series 6	Kr, 87.8	Rb, 85.4	Sr, 87.6	Ga, 70	Ge, 72.5	As, 75	Se, 79.2	Br, 80	
Series 7		Ag, 108	Cd, 112.4	Y, 89	Zr, 90.6	Cb, 94	Mo, 96		Ru, 101.7 Rh, 103 Pd, 106.5
Series 8	Xe, 128	Cs, 133	Ba, 137.4	In, 115	Sn, 119	Sb, 120	Te, 127.6	I, 127	
Series 9				La, 139	Ce, 140				
Series 10									
Series 11		Au, 197	Hg, 200						Os, 191 Ir, 193 Pt, 195
Series 12			Ra, 225				W, 184		
							U, 238.5		

The atomic weights in this table are in round numbers.

is followed by the strongly positive metal lithium, and with increasing atomic weight the metallic character diminishes, and the series ends with the most negative element known, fluorine.

The next series, No. 3, begins with neon, very similar to helium, but having a different spectrum, density and atomic weight, followed by sodium, in which the properties of lithium are repeated but with a difference, and ends with chlorine, in which the properties of fluorine recur in large measure. The second and third series form short periods, each containing eight elements.

The fourth series, however, of which argon is the first member, properly concludes with bromine at the end of Series 5; the two series form a long period containing eighteen elements. There is no sudden change in properties after the eighth member, manganese; instead, we have the three elements iron, nickel, and cobalt, which form a group by themselves, and are immediately succeeded by copper, without the intervention of a non-valent element corresponding to argon.

The properties of the elements in the fourth series recur with modifications, not in the ninth but in the nineteenth element. Thus krypton resembles argon, rubidium resembles potassium, and so on.

The sixth and seventh series combined, again, form a long period beginning with krypton and ending in iodine, the latter element being the nineteenth from bromine, to which it shows a marked resemblance.

In addition to this arrangement into nine groups, each of the groups I to VII inclusive is subdivided, according as the individual element comes in an odd or even series, disregarding hydrogen, and starting with the helium series as the first. Thus, in Group I the sub-groups are respectively Li, K, Rb, and Cs of the odd series, and of the even series Na, Cu, Ag, and Au. It is the practice with some chemists to push back the elements, copper, silver, and gold into

Group VIII, and to place sodium with lithium and the other alkali metals, with which it is obviously much more closely related than it is with copper.

The first two elements in each group, i. e. those in Series 2 and 3, are spoken of as *typical elements*. Thus in Group II beryllium and magnesium are 'typical'. A divergence in the properties of elements in the odd and even series of the same group begins after Series 2 and 3, and becomes greater the lower the elements occur in the table.

Thus the compounds of magnesium resemble those of calcium and zinc much more than do those of these two elements resemble one another. The same thing is noticeable in other groups.

The table shows that passing from left to right the atomic weights increase by a gradual, though not constant, amount, but the physical and chemical properties vary periodically. Take such a property as density in the solid state for the elements in Series 2. Density rises to a maximum with carbon and then falls, and the facts are similar for other series. Instead of studying the relation between density and atomic weight, Lothar Meyer selected the volume occupied by the gram-atom called the *atomic volume*, and he constructed a curve by plotting the atomic volumes of the elements as abscissae and atomic weights as ordinates. This curve is given at the end (facing p. 572).

It will be seen at once that elements which are chemically related occur at similar positions on the curve; thus the alkali metals occur at the maxima and on the ascending portions, and separated from the alkali metals by the inert gases of Group O occur the halogens.

Moreover, it will be noticed that the metallic elements occur at the maxima and on the descending curve, whereas the non-metals are found at the minima and on the descending portions.

The variation of such a chemical property as valency, which can be expressed numerically, is best seen in the

other table, a portion of which is printed below, giving the formulae of the halides and hydrides of the elements in Series 2 and 3.

O	I	II	III	IV	V	VI	VII	VIII
—	LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	OCl ₂	—	—
—	—	—	BH ₃	CH ₄	NH ₃	OH ₂	FH	—
—	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅	SF ₆	—	—
—	—	—	—	SiH ₄	PH ₃	SH ₂	ClH	—

The table on p. 317 also shows that the non-metals are mainly in the top right-hand portion, and that in a group of non-metals the higher the atomic weight the less non-metallic or acidic does the element become.

In a group of metals, the basic or metallic character increases with increasing atomic weight. The most basic metals occur on the left-hand side of the table; those on the right, such as Groups IV to VII, being more weakly basic and forming higher oxides which are acidic.

An important point to grasp about this classification is that a particular position in the scheme is associated with certain definite properties, so that it is possible, by a careful study of the properties of the elements surrounding a gap in the table, to assign with a fair degree of accuracy the properties of the element which would occupy the position if it were known.

Mendeléef actually predicted the properties of the elements gallium (Ga), germanium (Ge), and scandium (Sc) before their discovery, and his conclusions were amply justified.

The periodic system may also be used for the purpose of checking the valency of newly discovered elements. The properties of the element must be examined, and the group to which the new element belongs is thus found, and, knowing the valency and the equivalent weight, the correct atomic weight can be calculated.

Several anomalies occur in the system, notably in the cases of argon and tellurium. If these two elements are placed according to the magnitude of their atomic weights,

argon comes after potassium, and tellurium after iodine, thus displacing potassium and iodine from positions which on every other account they are bound to occupy. In the present state of our knowledge such exceptions are inexplicable, and we can only wait for the unravelling of the fundamental cause on which the relation between atomic weight and properties is based.

QUESTIONS ON CHAPTER XVII.

1. Examine the table on p. 317, and find out examples of Dobereiner's triads other than those already mentioned.

2. Explain the arrangement of the elements in the Periodic System, and show by reference to particular cases that the properties of elements vary periodically with their atomic weights.

3. What would be the valency of the element which would occupy the gap between barium and radium?

What do you suppose would be the formulae and the characters of its oxide, sulphate, and chloride?

4. A gap occurs in Group VB. Would the element be likely to form (a) a hydride, (b) an acid-forming oxide? If so, would the hydride be easily decomposed? What would be the formula of the acid-forming oxide?

5. From the table of solubilities, p. 458, draw curves for the solubilities of the chlorides, bromides, and iodides of Li, Na, and K.

6. Making use of the atomic volume curve (facing p. 572), calculate the densities, in the solid state, of the elements in Series 2 and 3. Where do the maxima and minima of density occur in the two series?

7. A new element is discovered. Its E.W. is 48. The metal is brittle, and a bad conductor, having a comparatively low M.P. It is oxidized by heating in air, and the oxide is rather volatile. It forms a hydride which is very unstable. Its chloride is easily decomposed by water, and its higher oxide is acidic, though weakly so. Where would this element be placed in the Periodic System?

CHAPTER XVIII

CARBON AND SOME OF ITS COMPOUNDS

Preliminary Questions.

1. What is produced when carbon burns in air? How is the product detected?
2. Indicate how you would proceed in order to discover whether a given (*a*) solid, (*b*) liquid, (*c*) gas contains carbon.
3. Name the solids, liquids, and gases which you have proved to contain carbon.
4. Explain briefly how (*a*) wood charcoal, (*b*) coke is made, and state the practical uses to which they are put.
5. Suggest a method for determining the equivalent of carbon with reference to oxygen.
6. What compound of carbon occurs in air? How does it get there, and what effect have plants and trees on it?
7. What is formed when carbon dioxide dissolves in water? What effect has the solution on blue litmus?
8. What type of substance would you expect to be formed when carbon dioxide is passed into aqueous solutions of alkalis, viz. lime, sodium hydroxide, potassium hydroxide? What name would you give to each substance?

Some commercial varieties of carbon and their uses.

It has already been pointed out that carbon exists in all animals and plants, and consequently in the majority of products obtained from these sources, such as wood, coal, oils, tallow, fats, food-stuffs, &c. In Chap. IX it was noticed that when carbonaceous substances were heated, either without air (p. 126) or in a restricted quantity of air, carbon was obtained. A very pure form of carbon can be made in this way by charring sugar.

Lamp-black is the purest commercial variety, and results from the incomplete combustion of tar, oils, or other hydrocarbons. The hydrogen burns, but the carbon is deposited, as soot, on blankets hung in cool chambers. It is used for black paint and printers' ink. Traces of hydrogen are removed by heating in a current of chlorine. Subsequent washing and drying gives pure amorphous carbon.

Gas-carbon is the hard grey stone-like deposit formed on the sides of the retorts of gas-works, simultaneously with coke. It is remarkable for its power of conducting electricity and is used for batteries and the terminals of arc-lamps. It contains about 95 per cent. of carbon.

Coke results from the dry distillation of coal as carried out in gas-works. It contains all the incombustible ash of the coal, and its composition varies considerably, averaging 91 per cent. of carbon. It is used as a fuel for stoves, since it burns without smoke, and is largely employed in iron smelting. This latter process consists in reducing the ore, which is an oxide of iron, by means of the carbon in coke.

Wood charcoal is obtained by the dry distillation of wood. Its composition varies with the wood used, and it contains the ash just as coke does, and about 85 per cent. of carbon. It is used as fuel and as a reducing agent. It is a porous solid and has the remarkable property of absorbing many times its own volume of certain gases, and on this account is used as a disinfectant in dissecting-rooms, &c. Owing to the presence of absorbed air it floats on water, but if the air is expelled it sinks.

Animal charcoal or bone-black is formed when bones are distilled. It only contains about 12 per cent. of carbon, but this is in a very finely divided condition spread over the calcium phosphate, which is the main constituent. Owing to its porosity and the fine state of division of the carbon, bone charcoal has the property of extracting colouring matters and other substances from their solutions. It is largely used for decolorizing sugar, for water-filters, &c.

The carbon in all these substances is non-crystalline or *amorphous*.

Exp. 1. To examine some common forms of amorphous carbon.

Required:—Substances named on p. 323; crucible, test-tubes, filter-paper, and funnel, weak solutions of copper sulphate, indigo, sulphuretted hydrogen, quinine sulphate.

DIRECTIONS. *A.* Examine specimens of the substances named on p. 323. **Note** their more obvious properties of colour, hardness, whether lighter or heavier than water, the effect of heating a *little* in an open crucible.

B. Half fill some test-tubes with the coloured solutions and add half a tea-spoonful of animal charcoal to each tube. Boil the solution and filter. **Note** whether the colour is retained by the liquid or not.

C. Half fill a test-tube with a *very dilute* solution of sulphuretted hydrogen. **Note** its smell. Add as much animal charcoal as in *A*. Warm gently and filter. **Note** whether the smell remains or not.

D. Pour a *weak* solution of quinine sulphate into a test-tube. Taste a drop. Add animal charcoal, boil and filter. Taste the filtrate, to find whether the quinine sulphate is still in solution.

LABORATORY RECORD. Arrange results of *A* in a schedule; observations in *B*, *C*, and *D*.

Exp. 2. To find whether charcoal will reduce copper oxide.

Required:—As above and in Fig. 69; hard-glass test-tube, lime-water.

DIRECTIONS. Powder a little wood charcoal, and mix with it about four times its bulk of copper oxide.

Introduce the mixture into a hard test-tube, fitted with an exit-tube as in Fig. 69.

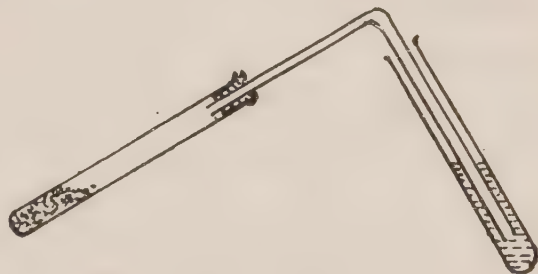


FIG. 69.

Arrange the exit-tube so that it just dips beneath some lime-water in a test-tube.

Heat the mixture strongly and **note** what takes place.

LABORATORY RECORD. Full observations.

Questions:—(i) Does charcoal reduce copper oxide?

(ii) What products are formed in Exp. 2?

(iii) How could you separate any excess of charcoal from the residue in the combustion tube? Carry this out, if approved.

PROBLEM (XVIII. 2). Read the paragraph below, and then find whether sugar, wax, naphthalene, contain carbon and hydrogen or not.

Detection of carbon and hydrogen in compounds. Just as the presence of hydrogen in a compound can be proved by heating it with dry copper oxide (p. 212) whereby water is formed, so carbon may be detected as in Exp. 2. The principle of this method is the same as in all chemical tests, viz.:—*the production of a substance of known composition from one of unknown composition.* It has already been applied in the cases of candle-wax, alcohol, coal, &c. (pp. 122-8), in which air was used as the oxidizing agent.

Many compounds contain hydrogen as well as carbon, so that the presence of both can be tested for at the same time.

The procedure consists simply in heating a *small* quantity of the given substance *X* with plenty of copper oxide, and observing whether carbon dioxide and water are produced.

If copper oxide + *X* give carbon dioxide and water, then *X* contains both hydrogen and carbon.

If copper oxide + *X* give water and no carbon dioxide, then *X* probably contains no carbon, but does contain hydrogen.

If copper oxide + *X* give carbon dioxide and no water, then *X* contains carbon and probably no hydrogen.

Exp. 3. To reduce metallic oxides on charcoal with a blow-pipe flame. *

Required:—A block of charcoal, blow-pipe; oxides of lead, antimony and bismuth; pestle and mortar, knife.

DIRECTIONS. Make a conical hole about 0.5 cm. deep in a block of charcoal, using a knife, and put in a *little* lead oxide.

Close the air-holes of the Bunsen burner, and turn the gas down so that the flame is about 5 cm. long.

Hold the blow-pipe firmly at the end near the nozzle with your right hand, and blow *gently* so as to deflect the flame downwards. Keep the nozzle just outside the flame.

Practise this until you can get a steady flame with a luminous tip; breathe through your nose.

Then take the charcoal in your left hand and hold it horizontally, so that the luminous tip strikes the lead oxide. Keep blowing *gently* for some time, and **note** what forms (a) in the hole, (b) round the edge.

When the metallic bead is cold, place it in a clean mortar, find whether it can be beaten out into a thin sheet or not (i.e. whether it is malleable or brittle), whether it can be cut with a knife, and whether it marks paper.

Try similar experiments with the oxides of antimony and bismuth.

LABORATORY RECORD. Diagram in section, showing how the flame strikes the oxide. Observations of changes noticed with each oxide used.

Questions:—(i) Why is it an advantage to use a luminous and hence a smoky flame?

(ii) What part does the charcoal play in the action?

(iii) What has been formed besides the lead? What has become of it? _____

This method is not applicable to all oxides, e.g. tin oxide, magnesium oxide, &c. Some of these can be reduced, if they are previously mixed with a more powerful reducing agent, and then treated as above, see Appendix.

Allotropic forms of carbon. The variety of carbon in charcoal, coke, lamp-black is called *amorphous carbon* to distinguish it from two crystalline varieties known as graphite and diamond. Pure sugar charcoal may be taken as typical of the amorphous variety, and if we compare its properties with those of graphite and diamond, such striking differences are observed that without experimental proof it would never have been suspected that all three were constructed from the same chemical element—carbon. Sir Humphry Davy first showed that diamond was carbon.

When a well-known element is found to exist in varieties which have physical properties widely differing from those of the common form, these varieties are called **allotropes**,* or allotropic forms of the element. Thus diamond and graphite are allotropes of carbon.

Sulphur, phosphorus, and oxygen also possess allotropic forms.

Graphite. This substance, also known as *black-lead* and *plumbago*, is found in certain rocks in Cumberland, Ceylon, &c., and is employed for making pencils, for protecting and polishing ironwork and for lubricating machinery, wooden screws, &c., where oil is objectionable. It is obtained in

* From Greek, meaning 'other forms'.

crystals—hexagonal plates—by dissolving the powdered substance in molten iron. On cooling and treating the iron with an acid, crystals are left.

Crystals of graphite are also obtained when charcoal is dissolved in molten iron, hence graphite appears to be a form of carbon. This is borne out by the fact that, although it burns with great difficulty, yet when it is strongly heated in oxygen it yields carbon dioxide and nothing else. That graphite consists only of carbon was unsuspected for a long time, since its physical properties are very different from those of pure amorphous carbon.

Diamond. This clear, transparent, and extremely hard stone, found in S. Africa, Brazil, &c., has no resemblance to either graphite or charcoal, but on heating in oxygen it yields carbon dioxide without any other product, beyond a mere trace of ash. It is therefore a variety of carbon.

Minute imperfect diamonds have been obtained artificially by Moissan. Sugar charcoal was pressed into a thick iron vessel and closed by a screw. This was heated in an electric furnace until soft. On removal from the furnace the surface of the iron was cooled by water, causing it to solidify and contract. In this way an enormous pressure was produced on the charcoal and semi-fluid iron in the interior. After slow cooling the iron was dissolved away in acid, and the residue was found to contain graphite, diamond, and many intermediate varieties of carbon. Separation was effected by placing these fragments in a heavy liquid. The diamonds sank, while the others floated.

The difference between the chief physical properties of pure sugar charcoal, graphite, and diamond can be seen from the following table:—

	Sp. g.	Optical properties.	Hardness.	Crystalline form.
Diamond .	3.5	Transparent, highly refractive and dispersive.	The hardest substance known, since it will scratch all others.	Octohedral crystals.
Graphite .	2.5	Opaque and black.	Soft, unctuous touch. Marks paper.	Hexagonal plates.
Pure sugar charcoal.	1.5	Opaque and black.	Soft powder. Friable in lumps.	Amorphous.

The evidence of their *chemical identity* is the fact that when equal weights of each are completely burnt in oxygen, equal weights of carbon dioxide are produced, but no other substance. The method of proving this will be found in Exp. 4.

***Exp. 4.** To determine the gravimetric composition of carbon dioxide.

The object of the experiment is to burn a known weight of carbon in oxygen and to collect and weigh the carbon dioxide produced. The apparatus is shown in Fig. 70.

H is a wash-bottle containing concentrated sulphuric acid.

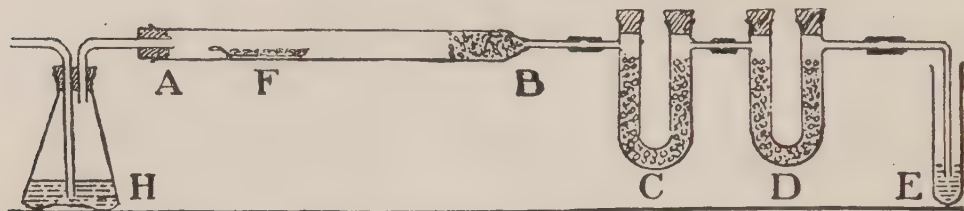


FIG. 70.

A B is a hard-glass tube drawn out at B, F is a porcelain boat, c and D are U-tubes packed with granular soda-lime, E is a test-tube containing a little sulphuric acid.

A little copper oxide or a piece of oxidized copper gauze is placed at B, to oxidize any carbon monoxide which may form to carbon dioxide.

Some pure dry sugar charcoal is put in the porcelain boat and weighed. The absorption-tubes c and D are also weighed and replaced. The boat is then put in the position shown in Fig. 70, and the cork at A pressed in.

The entrance-tube of the wash-bottle H is connected with the oxygen holder (another wash-bottle containing caustic soda solution being interposed if the oxygen is liable to contain traces of carbon dioxide) and a very slow stream of pure dry oxygen passed through the apparatus.

The copper oxide at B is first heated for a few minutes, and then F, until the charcoal begins to burn. Both B and F are heated until the charcoal has all disappeared.

The porcelain boat and the absorption-tubes are re-weighed as soon as they are cold.

* Demonstration.

$\frac{CO_2}{C} = 3.6$ for the different calculations

Weighings:—

Wt. of boat + charcoal = —g.	Wt. of soda-lime tubes after = —g.
Wt. of boat alone . . = —g.	Wt. of soda-lime tubes before = —g.
<i>Wt. of charcoal burnt . = —g.</i>	<i>Wt. of carbon dioxide formed = —g.</i>

Questions:—(i) What is the object of the wash-bottles containing caustic soda and sulphuric acid, and of the copper oxide?

(ii) What are the objections to a rapid stream of oxygen?

(iii) What is the percentage composition of carbon dioxide?

(iv) What is the equivalent weight of carbon?

When pure graphite or diamond are used instead of amorphous carbon, it is found that in each case 1 gram yields 3.6 grams of carbon dioxide.

***Exp. 5. To find the volumetric composition of carbon dioxide.**

Required:—As in Fig. 71; piece of recently heated charcoal, oxygen.

The object of the experiment is to burn carbon in a certain volume of oxygen and to find the volume of carbon dioxide produced at the same temperature and pressure.

Fill the U-tube with mercury to a point below the bulb as shown in Fig. 71.

Displace the air in the bulb with oxygen by placing a tube from the oxygen-holder inside it for a few minutes.

Put a *small* piece of recently heated charcoal in the coil of thin platinum wire c, which is joined to thick wires passing through a rubber stopper.

When the bulb is full of oxygen place the stopper in position.

Mark the position of the mercury below the bulb with a piece of gummed paper.

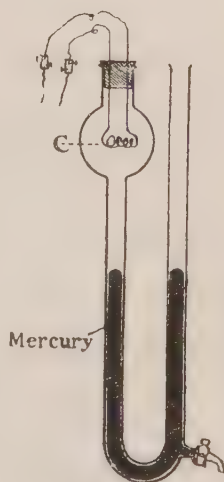


FIG. 71.

* Demonstration.

[Over.]

Connect the wires to the battery and so heat the charcoal by the red-hot platinum coil, for a few minutes. Stop the current and allow the bulb to cool. The gas in the bulb is now carbon dioxide. **Note** whether its volume (after cooling) is the same as that of the original oxygen.

LABORATORY RECORD. Diagram of the apparatus used : description of the method and observations made.

Questions :—(i) Why should the charcoal used have been recently heated under sand ?

(ii) What volume of carbon dioxide would result from burning charcoal in 1 litre of oxygen ?

The molecular formula of carbon dioxide.

The density of carbon dioxide is 22;

\therefore M.W. " " " $2 \times 22 = 44$.

By Exp. 4, 3.6 g. of carbon dioxide contain 1 g. carbon ;

\therefore 44 g. " " " $\frac{44}{3.6} = 12$ g. "

By Exp. 5, 1 mol. " " " 1 mol. oxygen ;

\therefore 44 g. " " " 32 g. "

Since the A.W. of oxygen is 16 and of carbon 12, it follows that CO_2 represents a molecule of carbon dioxide.

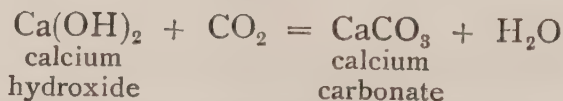
The equation for the synthesis of the gas therefore is—



Carbonates. It was found in Exp. 3, p. 167, that carbon dioxide dissolves to a slight extent in water, forming a feeble acid called carbonic acid,



Calcium carbonate, a salt of this acid, is formed when carbon dioxide is passed into a solution of calcium hydroxide, i.e. lime-water.



This carbonate is very abundant in Nature, limestone and chalk being chiefly composed of it. Its purest natural forms are marble, calc-spar or calcite, and Iceland spar, all of which have a crystalline structure.

Exp. 6. To examine the action of heat on carbonates.

Required :—Copper carbonate, marble, dehydrated washing soda, hard-glass tube (10 cm. long) as in Fig. 72 ; test-tubes, lime-water, iron wire, watch-glass, hydrochloric acid.

DIRECTIONS. *A.* Place a little dry copper carbonate in a hard tube and insert a *tightly* fitting cork and exit-tube as in Fig. 72.

The exit-tube dips into lime-water.

Heat the carbonate and **record** your observations.

Find whether the residual solid is a carbonate or not.

B Repeat *A*, using finely powdered marble and then washing soda previously dehydrated.

C. Take a *small* thin flake of marble and fasten a piece of iron wire round it.

Hold the end of the wire with tongs and heat the marble in the hottest part of the Bunsen flame for five minutes.

When cold, scrape off the outer portion on to a watch-glass. Transfer a little to a clean test-tube, shake with distilled water, and test with a red litmus-paper.

Decant off the clear liquid into another vessel and blow down a glass tube dipping into it.

Note the effect of this and the action on the litmus.

To the portion remaining on the watch-glass add two drops of hydrochloric acid, and **note** whether there is effervescence or not.

LABORATORY RECORD. Observations in *A*, *B*, and *C*.

Questions :—(i) What do you think the solid residue left in *A* is?

How could you find whether you are right or wrong?

(ii) Is marble decomposed on heating in a tube as in *B*?

(iii) What substance is left when marble is heated to a very high temperature?

(iv) What products result from heating washing soda?

PROBLEM (XVIII. 6). Investigate the action of heat on the carbonates of lead, zinc, and magnesium.

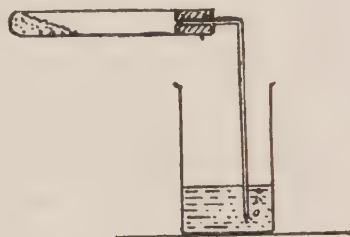


FIG. 72.

General action of heat on carbonates. The great majority of carbonates decompose on moderate heating, like copper carbonate. The carbonates of potassium and sodium (K_2CO_3 and Na_2CO_3) are not decomposed by heat.

The equation in the typical case of calcium carbonate is—



The evidence for the molecular formula $CaCO_3$ is given on p. 342.

The action of heat on a pure metallic carbonate is a general method for obtaining a pure metallic oxide.

Manufacture of lime. The process of decomposing calcium carbonate by heat has long been used in order to obtain lime from limestone—the commonest form of the carbonate. It is

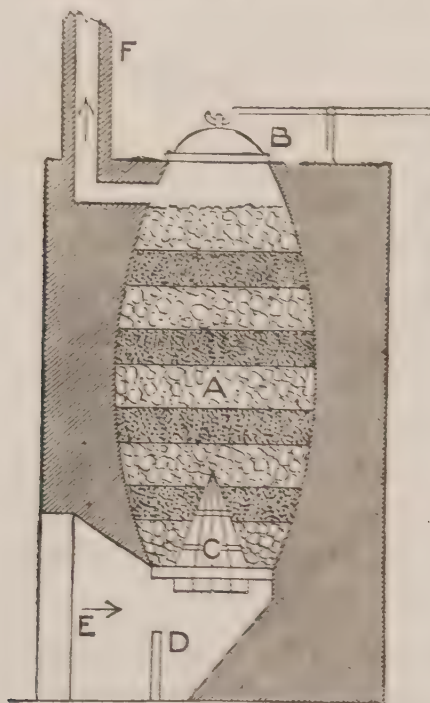


FIG. 73.

carried out in a kiln (Fig. 73), which is a furnace, generally made of stone, with an egg-shaped internal cavity. There is an opening at the bottom (E) for the admission of air, which passes up through a conical iron grid (c) on which alternate

layers of coal and limestone are placed. The heat of the burning coal decomposes the limestone, and the lime falls down through the grid while the oxide of carbon passes out through the flue (F) at the top. Fresh layers are added by removing the cover (B) as required, so that the process can be continued as long as may be desirable. The action may be expressed thus :—

On heating, *limestone* yields *lime* + *carbon dioxide*.



Handwritten notes:
On heating, limestone yields lime + carbon dioxide.
 $\text{CaCO}_3 + \text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2$

Exp. 7. To examine the action of mineral acids on carbonates.

Required:—Diluted mineral acids, marble, copper carbonate, washing soda, lime-water, test-tubes, and as in Fig. 74.

DIRECTIONS. *A.* Put a little marble, copper carbonate, and washing soda into separate test-tubes. Cover them with diluted *sulphuric acid* and **record** your observations on the action.

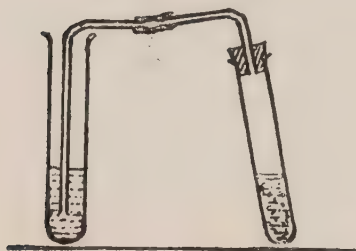


FIG. 74.

B. Repeat *A*, using diluted *nitric acid*, and **record** results.

C. Use diluted *hydrochloric acid*, but in this case place a well-fitting cork carrying a delivery-tube, as in Fig. 74, into the test-tube, as soon as the acid has been added.

Allow the gas evolved to bubble through lime-water.

Record your observations.

LABORATORY RECORD. Enter observations in a schedule.

Questions:—(i) What gas is produced in *C*?

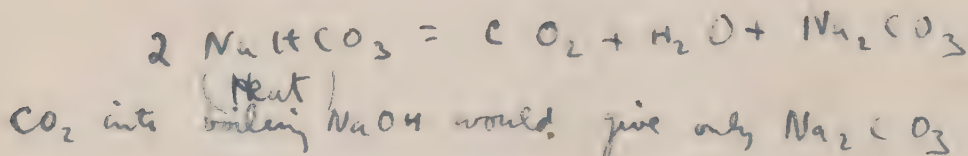
(ii) Which acid produces (*a*) the largest, (*b*) the smallest amount of gas from marble?

(iii) How may a carbonate be most readily recognized?

(iv) Write equations for the actions which occur in *C*.

PROBLEM (XVIII. 7). Discover whether *blackboard chalk*, *whitening*, *egg-shells* contain carbonates. Find what metals they contain by means of the flame tests, &c. (p. 137).

All carbonates act with hydrochloric acid in a similar way to those of Exp. 7.



Exp. 8. To prepare carbon dioxide from marble, and to examine its action on alkalis.

Required:—As above and in Fig. 75; hydrochloric acid (concl.), 3 gas-jars, caustic soda, lime-water, magnesium, sulphur, phosphorus.

Preparation. Fit up a flask as shown in Fig. 75; see that the cork is air-tight.

Slide a few pieces of white marble into the flask, cover these with water, and put in the cork. Pour 'strong' commercial hydrochloric acid down the funnel. Collect the gas by downward displacement of air. [A continuous supply of the gas can be obtained by using Kipp's apparatus.]

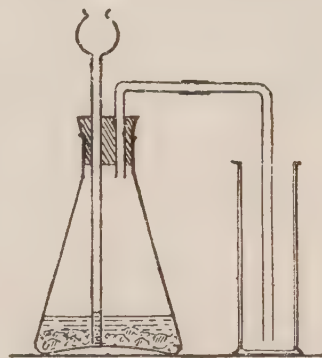


FIG. 75.

The chief *properties* of carbon dioxide have already been examined. Recapitulate these by writing them down in your notebook, re-testing any you are doubtful about. Then proceed as follows:—

A. Action on lime-water. Pass the gas for a few minutes through some clear lime-water in a beaker until a precipitate forms. Stir and immediately filter half the liquid, and find whether the precipitate is a carbonate.

Continue to bubble the gas through the remainder till it is clear again.

Take half this liquid, boil in a tube as shown in Fig. 74.

Note whether a gas is evolved; if so, test it.

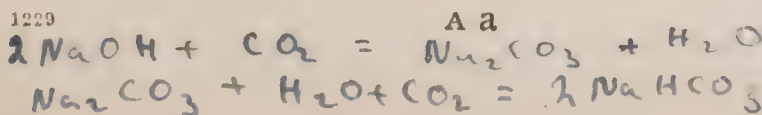
To the other half add more lime-water.

Collect the solid in each case, and test it for a carbonate.

B. Action on caustic soda solution. Invert a test-tubeful of the gas in a *small* beaker half filled with a solution of caustic soda. Shake the tube and **note** what happens.

Bubble more gas into the solution in the tube for some minutes; then add hydrochloric acid. **Note** and account for the result. [Caustic potash (KHO) acts similarly.] [Over.

1229



NaHCO₃ is less soluble than Na₂CO₃, so that if the caustic soda is strong a white p.p. (precipitate) of NaHCO₃ will be obtained.

*C. Action of burning magnesium, sulphur, and phosphorus.**
Take a jar of the gas and find whether these elements continue to burn or not. If they do, investigate the products and **note** all results.

N.B.—Keep the generating flask for Problem 1, below.

LABORATORY RECORD. Diagrams; complete observations. State the *properties* of carbon dioxide, as regards:—(a) colour, (b) smell, (c) solubility in water, (d) whether heavier or lighter than air. Action with (e) litmus, (f) burning taper, sulphur, and phosphorus, (g) burning magnesium, (h) lime-water, (i) caustic soda.

Write equations for (g), (h), and (i).

- Questions*:—(i) What is the white precipitate formed by the action of the gas on lime-water? Is it soluble (a) in pure water, (b) in water containing carbonic acid?
- (ii) What usually happens to a gas when its solution is heated?
- (iii) *Explain* the action of heat and of lime-water on the clear liquid in A.
- (iv) Should you expect (a) pure water, (b) water containing carbon dioxide in solution, to dissolve any limestone in passing over limestone rocks?
- (v) What is the origin of the incrustation or 'fur' which often forms in boilers and kettles?

PROBLEMS (XVIII. 8). 1. Filter and evaporate the liquid left in the flask (Fig. 75) after the action has ceased. Identify the solid obtained.

2. Devise a method for determining the weight of 1 litre of dry carbon dioxide at S. T. P. Submit full details for approval. [The weight of 1 l. of air at S. T. P. is 1.293 g.]

Carbon dioxide is now obtained on the **large scale** by utilizing the gas evolved during fermentation in breweries. The carbon dioxide is changed to a liquid, and finally to a solid, by cooling it under pressure. It is sold in the solid state and is used for the preparation of aerated waters.

* After the experiment, be careful to burn away the excess of phosphorus in a draught-chamber.

Exp. 9. Preparation of insoluble carbonates.

Required:—Solutions of calcium chloride, copper nitrate, sodium carbonate; beakers, porcelain basin, filter.

DIRECTIONS. Use 50 c.c. of 10 per cent. solutions of (*A*) calcium chloride, and (*B*) copper nitrate.

Heat the clear solution to boiling, remove the flame and cautiously add a solution of sodium carbonate until no more precipitate forms. (Avoid using great excess of the carbonate.)

Allow the precipitates to settle, decant the liquids and evaporate that from *A* to the crystallizing point. *Identify* the substance obtained.

Wash the precipitates by decantation three or four times, collect on a filter-paper* and wash until the wash-water is no longer alkaline. Dry *A* in air-oven at 120° C., and *B* in a steam-oven. Test a little of each to find whether they are carbonates. Cool both in a desiccator, and keep the calcium salt in it, as it will be wanted in a dry condition for Exp. 10.

LABORATORY RECORD. Short description and observations.

Questions:—(i) What substances are formed when calcium chloride is mixed with sodium carbonate? How were they identified?

(ii) Describe the carbonates of calcium and copper. Write equations for their formation.

PROBLEMS (XVIII. 9). 1. Determine the percentage loss in weight on heating *dry* copper carbonate strongly. Use a covered crucible.

2. Given solutions of *zinc sulphate, magnesium chloride, and iron chloride*, find whether the carbonates of these three metals can be prepared by the method of Exp. 9.

* Time may be saved by using a pump and rapid filtration apparatus of Fig. 50, p. 199.

Exp. 10. To find the percentage weight of carbon dioxide in natural and artificial calcium carbonate.

Required:—Pure marble or Iceland spar (powdered), calcium carbonate from Exp. 9; as in Fig. 76, desiccator, thread.

The object of the experiment is to find the weight of carbon dioxide evolved when a known weight of the carbonate is treated with acid.

A. Weigh a small dry flask (Fig. 76) alone, using the rider.

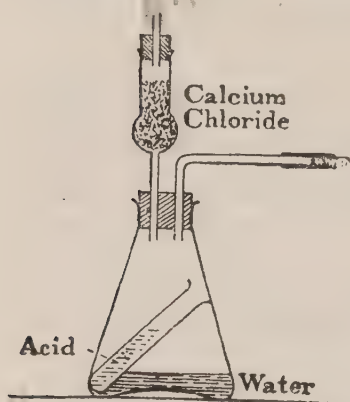


FIG. 76.

Add not more than 1.5 g. of the powdered marble and weigh again exactly.

Cover it with a thin layer of water. Nearly fill the test-tube with strong hydrochloric acid. Lower it into the flask by a thread, without spilling any, and then fix the cork carrying the drying-tube.

(It is advisable to put some dry copper-sulphate pumice above the calcium

chloride to prevent the escape of acid fumes. Refer to Appendix.)

Weigh the whole exactly and **record** all weighings.

Tilt the flask till some acid runs out of the tube on to the carbonate. Repeat, when the effervescence slackens, until no more solid remains.

Warm the flask *very gently* for a minute or two to expel any gas which has dissolved in the water.

Then displace the gas which still remains in the flask by removing the glass plug from the right-angled tube and sucking air through a rubber tube attached to the drying-tube.

Replace the plug, remove the rubber tube, and reweigh the whole apparatus.

B. Use the artificial calcium carbonate made in Exp. 9, and repeat *A*, but use fresh materials in the drying-tube.

LABORATORY RECORD. Diagram of apparatus used.

		Natural.	Artificial.
Weight of flask + carbonate	=	— g.	— g.
" " " alone	=	— g.	— g.
<i>Weight of carbonate taken</i>	=	(X) g.	— g.
Weight of whole apparatus before	=	— g.	— g.
" " " " after	=	— g.	— g.
<i>Weight of carbon dioxide</i>	=	(Y) g.	— g.

The percentage weight of carbon dioxide in the sample is

$$\frac{Y}{X} \times 100.$$

Give a list of the *possible errors* in performing the experiment; and state whether they would make the final result too large or too small.

Questions:—(i) Is the percentage of carbon dioxide obtained from the natural carbonate approximately the same as that from the artificial substance or not?

(ii) What is the law of definite proportions? Does your result support it or not?

Percentage composition of calcium carbonate. The result of Exp. 10 should show that the percentage of carbon dioxide in natural and artificial calcium carbonate is the same, and thus provides an example of the Law of Definite Proportions (p. 233).

Accurate experiments show that 100 g. of the carbonate yield 44 g. of carbon dioxide. Exp. 6 has shown that the carbon decomposes on heating, yielding calcium oxide (lime) and carbon dioxide.

Therefore 56 g. of calcium oxide combine with 44 g. of carbon dioxide, and yield 100 g. of calcium carbonate.

Now, Exp. 4 shows that 44 g. of carbon dioxide contain 12 g. of carbon and 32 g. of oxygen, and it can be shown that 56 g. of lime contain 40 g. of calcium and 16 g. of oxygen.

Thus the percentage composition of the carbonate is determined, and the result may be expressed as follows:—

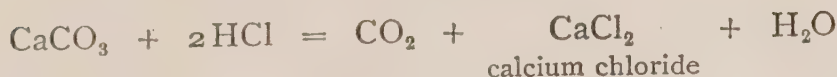
Calcium	.	.	.	40
Carbon	.	.	.	12
Oxygen	.	.	.	48
Calcium carbonate	.			<u>100</u>

It is by methods similar to this that the percentage composition of many complex substances is ascertained.

Assuming the atomic weights of calcium, carbon, and oxygen are 40, 12, and 16 respectively, the simplest formula is CaCO_3 .

Equations for reactions involving carbon dioxide.

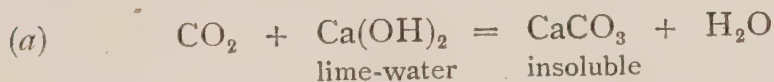
The *preparation from marble* (p. 337).



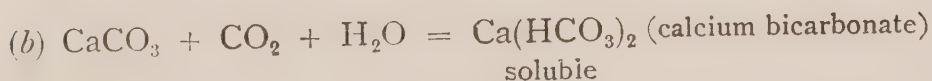
Action on *water*. Carbonic acid forms in solution, but it has never been obtained free from water.



The action on *lime-water* (p. 337) results in the formation of calcium carbonate, which is precipitated.



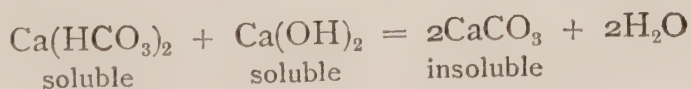
On passing more gas into the liquid, the precipitate dissolves, since soluble calcium bicarbonate forms.



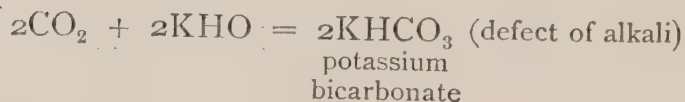
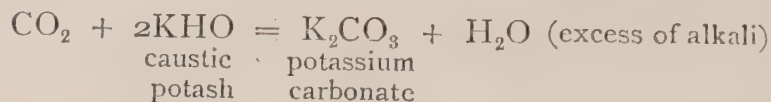
On boiling the bicarbonate solution, carbon dioxide is expelled and the original precipitate re-forms.



On adding lime-water to the bicarbonate solution.

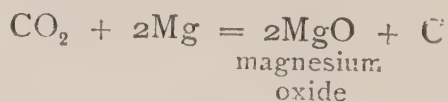


Action on *caustic soda and potash* (p. 337). There are two stages, as in the case of calcium hydroxide above, but both carbonates are soluble.



A solution of caustic potash or caustic soda is used to absorb carbon dioxide in gravimetric experiments.

Decomposition by *magnesium* (p. 338).



Exp. II. To find what is formed when carbon dioxide is absorbed by a solution of sodium carbonate (washing soda).

Required:—Carbon dioxide generator, small flask, sodium carbonate, platinum wire, unglazed plate, test-tubes, litmus.

DIRECTIONS. Arrange a small flask like D in Fig. 65, and put into it *not more than* 20 c.c. of *saturated* sodium carbonate solution. Weigh the whole. Pass carbon dioxide from a generator through a flask of water, to remove traces of acid, and then through the solution for an hour or two, and until a solid has formed. Reweigh the flask and contents.

Pour the liquid away and collect the solid on an unglazed plate. After drying in a desiccator do the following experiments, *both with it and with some ordinary sodium carbonate:—*

(a) Try the flame test for both (p. 137).

(b) Add hydrochloric acid to each and identify the gas evolved (Fig. 74).

(c) Heat in a hard tube (Fig. 69), and test any gas evolved. What is the solid residue?

(d) Boil a little of each with water, in the tubes used for (b), and discover whether carbon dioxide is given off.

LABORATORY RECORD. Weighings; full observations with a description of the tests.

Questions:—(i) Do both the substances used in (a), &c., contain sodium? Are both carbonates?

(ii) Has the original sodium carbonate absorbed carbon dioxide? State the evidence.

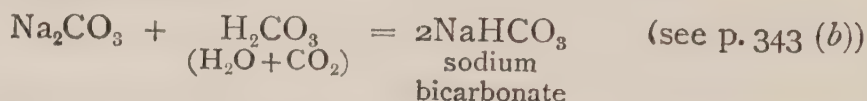
(iii) What three products are obtained by heating the new substance (*viz.* sodium bicarbonate or baking soda)? Write an equation.

(iv) Write an equation for the original reaction

PROBLEM (XVIII. II). Add a solution of *sodium bicarbonate* to one of *magnesium sulphate*. **Note** any change and then boil. Investigate the change which takes place. Write an equation for the action; NaHCO_3 and MgSO_4 are the formulae for the reacting substances.

Bicarbonates. The sodium bicarbonate made in Exp. 11 obviously contains a larger proportion of carbon dioxide than ordinary or *normal* sodium carbonate, since it was made by the union of the two in the presence of water. It may be considered as a compound of carbonic acid with the normal carbonate, because on heating it yields water, carbon dioxide, and the normal salt. This change takes place even when the bicarbonate is heated with water.

The equations are :—



On heating :—



Hardness of water. It is customary to speak of natural spring or river waters, which fail to give an immediate lather with soap, as 'hard' waters. Such waters cause the hands to feel rough, and require the use of more soap to produce a lather than in the case of a 'soft' water. At the same time a quantity of a white curdy substance is formed which floats at the surface of the water. Since rain and distilled water are perfectly soft, hardness must be due to the presence of dissolved substances.

It is found that the water from limestone districts can be rendered softer (not always quite soft) by boiling, and that a crust of calcium or magnesium carbonate is left on the sides of the kettle or other vessel in which it is heated. Since calcium and magnesium bicarbonates are likely to be formed by the action of the carbon dioxide of the air and water on limestone (calcium and magnesium carbonates), there can be little doubt that the hardness is partly due to these substances.

Water which can be softened by boiling is said to be *temporarily* hard; it can also be softened by adding the proper quantity of lime to the reservoirs. The lime decomposes the calcium bicarbonate and a precipitate of insoluble

calcium carbonate sinks to the bottom (see equations, p. 343). Water not softened by boiling or by lime is said to be *permanently* hard.

The rôle played by soap in the softening of water will be better understood when Exps. 12 and 13 have been done.

Exp. 12. The action of hydrochloric acid on hard soap.

Required:—Hard (yellow) soap, beaker, hydrochloric acid, sodium hydroxide solution, alcohol, unglazed plate, platinum wire.

A. Cut up the soap into shreds, and put it into a beaker half full of boiling distilled water. Stir until the soap is dissolved. (Keep half for Exp. 13.)

Add hydrochloric acid until no further milkiness is produced. Boil; then cool the beaker in a trough of water. Remove the cake from the surface of the liquid, and press it on blotting-paper to dry it. Then place it in a dry beaker, cover with alcohol (industrial spirit), and heat on a steam-bath until the solid has dissolved. Test with red and blue litmus-paper. Cover the beaker with a filter-paper and set it aside until the dissolved solid has crystallized out.

B. Pour off the alcohol and scrape *the solid* on to an unglazed plate, and leave until it is quite dry.

Find whether it melts below 100°C. , and heat a little to redness on porcelain. Compare the effect of treating soap in a similar manner and test the residue from soap by the flame coloration.

Find whether it contains carbon and hydrogen (p. 325).

Heat a little with sodium hydroxide solution and **note** the result after shaking.

LABORATORY RECORD. Description; observations in *A* and *B*.

Questions:—(i) Is the solid obtained in *A* soluble in water? Is it an acid? Does it contain carbon and hydrogen?

(ii) What forms when it is heated with sodium hydroxide?

[Over.]

- (iii) Does it leave any residue when heated on porcelain? Compare it with soap on this point.
- (iv) What is the chemical character of soap, supposing that double decomposition takes place between it and hydrogen chloride?

Exp. 13. To mix solutions of soap and calcium chloride and to examine the product.

Required:—Soap, calcium chloride solution, beakers, platinum wire.

Make a solution of soap as in Exp. 12, and add a solution of calcium chloride until no further change is noticed.

Boil, and separate the solid from the liquid. Break it up and boil with distilled water so as to remove any excess of calcium chloride. Dry it on blotting-paper.

Test a small portion of the solid for calcium.

Boil the rest with hydrochloric acid and **note** whether the same substance is obtained as when soap is boiled with this acid.

LABORATORY RECORD. Description and observations.

Questions:—(i) Does the solid contain calcium?

(ii) Is there any reason to regard the solid as a soap like yellow soap, but an insoluble one?

Soap and its action with hard water. Exp. 12 showed that soap by double decomposition with hydrochloric acid gave an acid containing carbon and hydrogen (it also contains oxygen) and sodium chloride. All soaps are in fact salts of what are known as fatty acids.

These fatty acids, such as stearic and palmitic, are present in combination in fats and oils; soaps are made from the latter by boiling with caustic alkalis, glycerine being obtained as a by-product. The action of sodium hydroxide on fat may be represented thus:—

Fat + sodium hydroxide give sodium stearate (soap) + glycerine.

Recognizing then that soap is a salt, its behaviour with a calcium salt in solution can be easily understood. For

example, sodium stearate and calcium chloride, both of which are soluble, react and give (by double decomposition) insoluble calcium stearate and soluble sodium chloride.

We are now in a position to understand the rôle played by soap in the softening of water containing calcium bicarbonate; the following action takes place:—

Sodium stearate + *calcium bicarbonate* give *calcium stearate* + *sodium bicarbonate*.
(soluble) (insoluble)

As soon as all the calcium bicarbonate is changed to calcium stearate the water is soft.

Hardness which is not due to the presence of bicarbonates, but to the sulphates and chlorides of calcium and magnesium, is known as **permanent hardness**. These salts are not precipitated by boiling, but on addition of normal sodium carbonate their insoluble carbonates are formed.

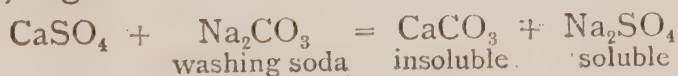
Hence 'permanently' hard water is softened by addition of sodium carbonate—whence the name 'washing soda'. The action of the above salts on soap is similar to that of their bicarbonates. Thus:—

Calcium sulphate + *sodium stearate* give *calcium stearate* + *sodium sulphate*.
(soluble) (soluble) (insoluble) (soluble)

Calcium sulphate + *sodium carbonate* give *calcium carbonate* + *sodium sulphate*.
(soluble) (soluble) (insoluble) (soluble)

The presence of dissolved sodium salts, e.g. common salt, does not make a water hard, because *all sodium salts are soluble*. They therefore form no precipitate on addition of soap. Sea water is very hard, not on account of the common salt it contains, but on account of calcium and magnesium salts.

A given sample of water may contain both the bicarbonates and also the sulphates of magnesium and calcium. In such a case the 'hardness' of the water is partly temporary and partly permanent. Boiling will not soften it completely; subsequent addition of washing soda will be necessary, e.g.:—



The calcium is precipitated as carbonate, leaving the water with sodium sulphate in solution. As the latter does not react with soap, the water is now completely softened, provided that it had previously been boiled to decompose the soluble bicarbonates of calcium and magnesium.

Exp. 14. To make soap by the saponification of lard.

Required:—Sodium hydroxide, lard, alcohol (industrial spirit), saturated salt solution.

DIRECTIONS. Put 50 c.c. of alcohol (industrial spirit) into a beaker, add a little water, and half a stick of caustic soda. Heat on a water-bath till the soda is dissolved.

Melt the lard in a basin and add it to the alkaline solution in small quantities at a time.

Continue heating till the oil has disappeared, and pour the liquid into five times its bulk of brine. The soap is thus 'salted out' and on standing rises to the surface.

To separate it from the liquid, which consists of a solution of excess of alkali, alcohol, glycerine and brine, filter through linen (a duster serves well), and squeeze out the superfluous moisture.

Boil some of the soap with hydrochloric acid and see whether the fatty acid is obtainable.

Find what metal it contains.

Any reaction by which the salts of fatty acids with organic radicals, such as glyceryl, are decomposed by the action of an alkaline hydroxide is called **saponification**.

LABORATORY RECORD. Description and observations.

Questions:—(i) What was the object of (a) the alcohol, (b) the brine?

(ii) Assuming that the chemical action only involved the lard and sodium hydroxide, what conclusion can be drawn about the probable composition of glycerine?

Natural waters. Waters obtained from natural sources may roughly be divided into four classes, depending on the quantity and kind of dissolved matter they contain.

I. *Rain water* is the purest and only contains dissolved gases from the air and minute traces of dust.

II. *River water* contains dissolved and suspended solids. Their quantity and kind depend on the sort of soil and rock through which the river and its tributaries have passed. The majority contain bicarbonates and sulphates of calcium and magnesium and chlorides of magnesium, sodium, or potassium.

III. *Spring water* is of two kinds—*fresh spring water* and *mineral spring water*. The former is similar to river water, sometimes purer, sometimes not. The latter contains less common substances, e.g. compounds of iron (chalybeate water), of magnesium (magnesia water), of sulphur, as at Harrogate, Bath, and Cheltenham. Many of these waters are hot, and most contain a large amount of common salt.

IV. *Sea water* contains about 36 parts per thousand of dissolved solids, of which 26 are common salt. Rivers pour their water into the sea, where the pure water evaporates, leaving the solids, which keep increasing in quantity. Inland seas, like the Dead Sea, often contain a much larger proportion of dissolved matter.

Chemically pure water is obtained from any of these sources by (a) filtering from suspended solids ;

(b) distilling from non-volatile dissolved solids (see p. 33), rejecting the first fifth of the distillate, which contains most of the volatile organic matter, and leaving the last fifth in the still ;

(c) redistilling, after adding some Condylé's fluid and caustic potash to oxidize any volatile organic matter which remains. When oxidized, most organic impurities are rendered non-volatile. (The first portion of this distillate is also rejected.)

The 'still' used for (b) and (c) should be coated inside with tin, since other common metals act chemically on some waters.

For *drinking purposes*, none of the substances mentioned as occurring in fresh spring and river water are particularly harmful. What makes water unwholesome for drinking is the presence of decaying organic matter, such as sewage. In flowing rivers this soon gets oxidized by the air dissolved in the water, and then it is no longer (or at any rate less) harmful. But polluted water, if drawn from ponds or shallow wells, has little or no chance of being oxidized, and is to be avoided.

Moderately good drinking-water is sometimes made harmful by household filters which are not kept clean. If the filtering material is not constantly renewed, minute organisms will germinate there rapidly, and contaminate all water subsequently passed through it.

Action of lead. Another source of danger arises from compounds of lead which are dissolved by water conveyed in lead pipes. Pure water (containing only dissolved air), on contact with lead, forms lead hydroxide, which is slightly soluble; very soft water containing small traces of vegetable matter (e.g. moorland water) dissolves lead much more rapidly. The presence of calcium bicarbonate, however, almost entirely prevents the solution of lead compounds. It is sometimes necessary to filter these soft and very pure waters through chalk, to allow them to dissolve enough calcium bicarbonate to prevent them from dissolving lead.

* **Exp. 15.** The action of red-hot charcoal on carbon dioxide.

Required :—Carbon dioxide generator; as in Fig. 77; lime-water, taper.

A hard combustion tube is packed with wood charcoal and heated to redness in a furnace as shown in Fig. 77.

A very *slow* current of carbon dioxide is passed through it and the product is collected over water.

[If necessary a wash-bottle containing caustic soda solution can be interposed between the combustion tube and the trough to absorb any unchanged carbon dioxide.]

When the jar is full, it is closed by a plate and shaken with a little clear lime-water. **Note** whether a precipitate forms or not.

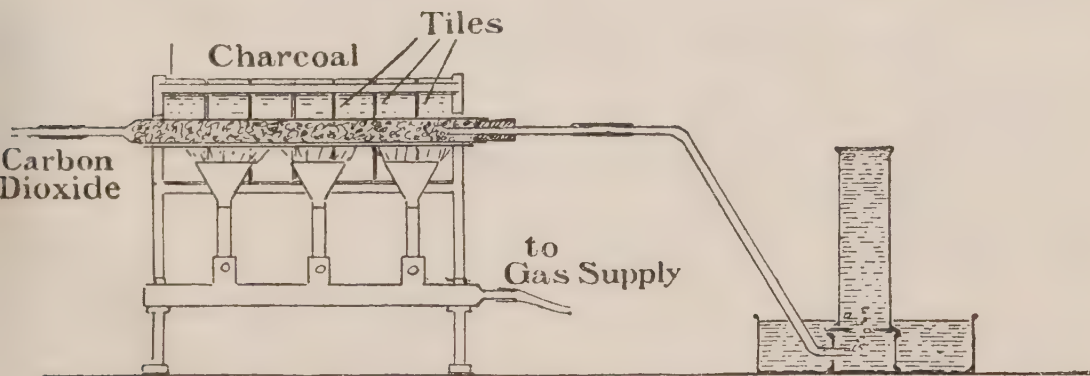


FIG. 77.

Precaution ;—*The gas is very poisonous, and must not escape into the air.*

Then a lighted taper is applied to the mouth, and after observing the effect, it is again shaken with the lime-water.

Note what happens in each case.

LABORATORY RECORD. Diagram and brief description.

Questions :—(i) Has the new gas any effect on lime-water?

(ii) What substance is formed when it burns in air?

(iii) Does the gas contain a larger or a smaller proportion of oxygen than carbon dioxide?

* Demonstration.

[Over.]

- (iv) Is the gas a reduction product of carbon dioxide?
 (v) Would you expect the new gas (called **carbon monoxide**) to be a reducing agent? Give a reason.

If a slow current of *air* be passed over the charcoal, the same product (carbon monoxide), mixed with nitrogen, is obtained. This mixture, which is made on the large scale, is called **producer gas**.

When steam is passed over red-hot coke a mixture of carbon monoxide and hydrogen results, and is known as **water-gas**. The passage of a mixture of steam and air over heated coal results in the formation of **Mond gas**. These gaseous mixtures are now largely used in manufactories, as sources of heat and as reducing agents.

Exp. 16. To prepare carbon monoxide from oxalic acid and to examine its properties.

Required:—As in Fig. 78; oxalic acid and conc. sulphuric acids, caustic soda solution, 2 gas-jars, lime-water, taper, hard tube, copper oxide.

Preparation. Set up apparatus as shown in Fig. 78, and see that it is air-tight.

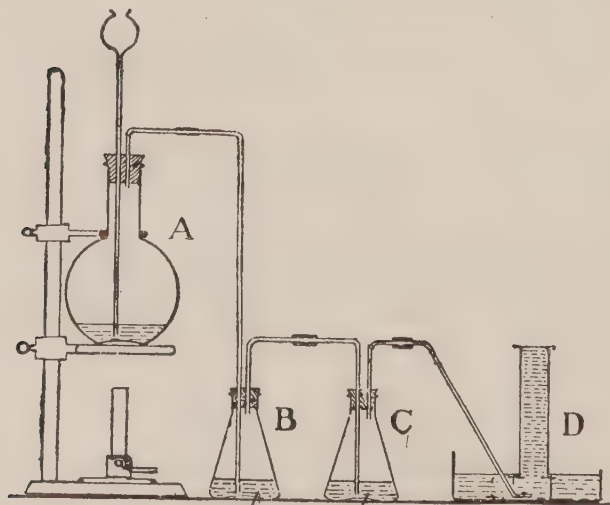


FIG. 78.

Place a *strong* solution of caustic soda in B and C. Detach the flask A and slide into it about 20 g. of oxalic acid crystals.

Re-cork it and pour about 60 c.c. of concentrated sulphuric acid down the funnel. Warm gently and **observe** the effect.

Precautions:—(1) *Avoid a rapid evolution of gas by turning the lamp low, but do not allow the evolution to stop.*

Normal Sodium Carbonate would be formed.



(2) *Avoid breathing the monoxide ; when not being used put the end of the delivery-tube in the air-hole of a lighted Bunsen lamp.*

N.B.—A mixture of the two oxides of carbon is formed ; the dioxide is absorbed by caustic soda, unless the gas bubbles through too quickly.

Properties. First collect a test-tubeful of the gas and find whether it is air or carbon monoxide. Collect one jarful of the gas and perform a test with it while the other is being filled. (Get everything you require ready first.)

(a) Shake with lime-water. (b) Apply a lighted taper.

(c) Find whether the gas is appreciably soluble in water.

(d) Find what is formed when the gas burns in air.

(e) Find its action on heated copper oxide contained in a hard tube. Let the excess of the monoxide burn at the mouth of the tube.

LABORATORY RECORD. Diagram ; complete observations.

Questions :—(i) Compare the properties of the two oxides of carbon in two parallel columns.

(ii) Which do you think contains the largest percentage weight of oxygen, and why ?

(iii) Is the monoxide a reducing agent ? Give reasons.

PROBLEMS (XVIII. 16). 1. Devise a method for determining the proportion by volume which the carbon dioxide bears to the monoxide in the mixture obtained from the flask A (Fig. 78). If the method is approved, carry it out.

2. Prepare carbon monoxide from *formic acid*. No dioxide is formed ; therefore flasks B and C are not needed.

* **Exp. 17.** To determine the volumetric composition of carbon monoxide.

Required:—Eudiometer as on p. 226, and Fig. 79; mercury, glass mortar, carbon monoxide, oxygen, caustic potash, thick rubber tube.

The object of the experiment is to find the volume of oxygen with which a known volume of carbon monoxide will combine, and also the volume of dioxide produced.

The principle of the method is to explode a known volume of carbon monoxide with excess of oxygen, then to measure the contraction due to absorption of the carbon dioxide by caustic soda or potash and to find the volume of oxygen left.

Introduction of the gases into the eudiometer. Each of the gases may first conveniently be collected by displacement over mercury in the laboratory tube (Fig. 79) and then be transferred to the explosion tube for measurement.

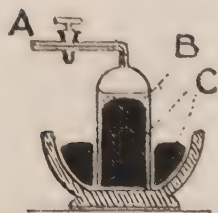


FIG. 79.

Having attached a piece of thick-walled rubber tubing to the exit A, the laboratory tube is completely filled with mercury c and fixed in a glass trough as shown in Fig. 79.

The trough is supported on a stand so that the explosion and laboratory tubes can be joined by means of the rubber tube, inside of which the ends of the glass tubes A and K are brought close together.

About 15 c.c. of carbon monoxide, made from formic acid, are passed into the laboratory tube, and from thence transferred to the explosion tube, where its volume is measured under known conditions. About the same volume of oxygen is added and the volume of the mixture is read.

Explosion and measurement of the residual gases. The explosion is carried out as in Exp. 10, p. 228, and when the gases have cooled to the temperature of the water-jacket the new volume is read.

* Demonstration.

Some caustic potash solution B is now passed up into the laboratory tube by means of a bent pipette, and the gas is driven from the explosion tube into the laboratory tube, where absorption of the carbon dioxide takes place.

The residual gas is then passed back into the explosion tube and its volume is measured.

To ensure that complete absorption shall take place, it is again passed into the potash. The total contraction gives the carbon dioxide formed, whilst the residual gas is the unused oxygen.

Providing that there are no changes in the height of the barometer or in temperature during the experiment, corrections for pressure and temperature are unnecessary.

Readings:—

Volume of carbon monoxide taken	= (<i>k</i>) c.c.
Volume of carbon monoxide and oxygen	= — c.c.
Volume of oxygen taken	= (<i>p</i>) c.c.
Volume of oxygen left + carbon dioxide formed	= (<i>x</i>) c.c.
Volume after absorption of carbon dioxide	= (<i>y</i>) c.c.
Volume of carbon dioxide formed	= (<i>z</i>) c.c.

k c.c. of carbon monoxide combine with $p - y$ c.c. of oxygen and give *z* c.c. of carbon dioxide.

The two oxides of carbon. These oxides form another example of two elements combining together in different proportions, producing compounds with very different properties. The results of Exp. 17 show that—

1 vol. monoxide + $\frac{1}{2}$ vol. of oxygen *yield* 1 vol. dioxide.

Since 1 vol. of the dioxide contains (Exp. 5) 1 vol. of oxygen;

\therefore 1 vol. of monoxide contains $\frac{1}{2}$ vol. of oxygen.

From this the *gravimetric* proportion of carbon to oxygen in the monoxide may be deduced, assuming that of the dioxide is known (Exp. 4), for half a volume of oxygen has half the weight of one volume.

1 g. carbon + 2.6 g. oxygen *yield* 3.6 g. dioxide (Exp. 4);

\therefore 1 g. carbon + 1.3 g. oxygen *yield* 2.3 g. monoxide.

Expressed in percentages we have :—

	<i>Dioxide</i>	<i>Monoxide</i>
Carbon	27.27	42.85
Oxygen	72.72	57.14
	<u>99.99</u>	<u>99.99</u>

It will be noticed that the ratio of the combining volumes of carbon monoxide to oxygen (viz. 1 : $\frac{1}{2}$ or 2 : 1) is a very simple ratio; and that the ratio of the volume of the monoxide to that of the dioxide produced (viz. 1 : 1) is also very simple, affording another example of Gay-Lussac's Law.

Further, for the *same* weight of carbon the weights of oxygen are in a simple ratio, viz. 2.6 : 1.3 or 2 : 1. This is a further illustration of the Law of Multiple Proportions.

Molecular formula of carbon monoxide. From the percentage composition given above, we see that the ratio of—

$$\frac{\text{number of carbon atoms}}{\text{number of oxygen atoms}} = \frac{42.85 \div 12}{57.14 \div 16} = \frac{42.85 \times 16}{57.14 \times 12} = \frac{4(171.4)}{4(171.4)} = \frac{1}{1}.$$

i.e. there is an equal number of each kind of atom in one molecule of the monoxide.

\therefore the formula is C_nO_n , and the M. W. is $n(12 + 16) = 28n$.

Now, the density of the monoxide is 14;

\therefore its M. W. is 28;

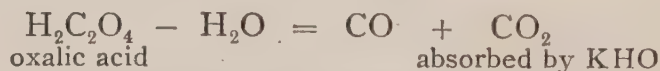
$\therefore n = 1$, and CO is the molecular formula.

Equations involving carbon monoxide.

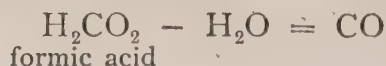
Formation by reduction of carbon dioxide (p. 353):—



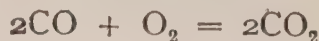
Preparation from oxalic acid (p. 354):—



The sulphuric acid combines with the elements of one molecule of water from one molecule of oxalic acid. A similar dehydration occurs when sulphuric reacts with formic acid:—



Combustion in air or oxygen:—



Other compounds of carbon. More compounds of carbon are known than of any other element, and a distinct branch of Chemistry (Organic Chemistry) is devoted to their study. There are, for instance, several hundred compounds of carbon and hydrogen; each of these has a large number of derivatives. In this book we can only deal with very few.

One of the best-known hydro-carbons is *methane* or *marsh gas*, which results from the decomposition of vegetable matter in ponds. On stirring the mud the gas is disengaged, and may be collected in bottles. It was in this way that Dalton collected it and used it for many important experiments. It forms, like all gaseous hydro-carbons, a very explosive mixture with air. Owing to its occurrence in coal-mines, where it often causes explosions, it is also known as 'fire-damp'.

Benzene is another common hydro-carbon obtained by the fractional distillation of coal-tar. *Turpentine* is a liquid hydro-carbon obtained from pine-trees. *Petroleum* or *paraffin oil* is a mixture of several liquid hydro-carbons; these occur in springs, notably in Pennsylvania. *Vaseline* and *paraffin wax* are mixtures of solid hydro-carbons.

Coal-gas is a mixture consisting of about 50 per cent. of hydrogen, 35 per cent. of marsh gas, 3 to 6 per cent. of illuminating hydro-carbons, together with small quantities of other gases.

Recently, owing to the introduction of the electric furnace, a large number of compounds of carbon with metals have been obtained in considerable quantity. These compounds are called *carbides*. For example, if lime (or limestone) mixed with coke is heated in an electric furnace, solid calcium carbide is formed. When this substance is brought in contact with water, a compound of hydrogen and carbon, called acetylene, results. This gas is now used as an illuminant.

Exp. 18. To prepare methane from sodium acetate.

Required:—Sodium acetate, powdered soda-lime, long iron or copper tube, &c., bromine water.

DIRECTIONS. Place about 30 grams of sodium acetate on a clean sand-bath and heat to expel water of crystallization. It will melt, then froth up, and finally melt again. Allow it to get solid and crush in a mortar. Mix with twice its bulk of soda-lime powder and fill about a third of a long iron tube with the mixture.

Fix the cork and delivery-tube, and clamp so as to slope slightly up towards the cork.

Heat with a *large* Bunsen flame. Collect the gas as soon as air has escaped in four or five jars.

Test with a taper. **Note** colour, smell, whether soluble in water, heavier or lighter than air, and any other obvious properties.

Find out whether carbon dioxide is formed by the combustion of the gas.

Add some bromine water to one jar and **observe** whether any change takes place.

LABORATORY RECORD. Diagram; list of observed properties.

Questions:—(i) How could you find whether the gas contains hydrogen?

(ii) Given that its density is 8, and that it contains 25 per cent. hydrogen and 75 per cent. carbon, deduce its molecular formula.

(iii) Write an equation for the change produced by burning the gas.

(iv) How many c.c. of oxygen are required to burn 1 c.c. of the gas completely?

Exp. 19. Preparation and properties of ethylene.

Required:—As in Fig. 80; dehydrated alcohol, conc. sulphuric acid, bromine water.

DIRECTIONS. Cover the bottom of the flask (500 c.c.) with sand, and pour down the funnel a mixture of alcohol with five times its volume of concentrated sulphuric acid.

Heat it on a sand-bath with a small flame, and when air is expelled collect five jars of the gas. Stop heating when the mixture becomes black.

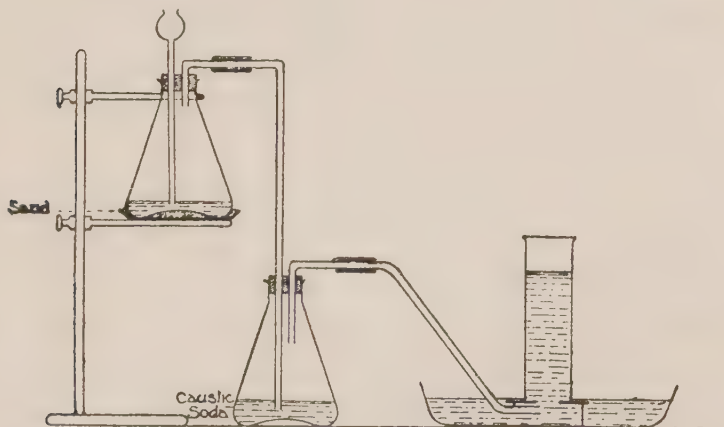


FIG. 80.

Note the colour. The smell is likely to be due to impurities. Test with a taper. **Notice** whether it is lighter or heavier than air.

To one jar add bromine water and **observe** whether any change takes place. Find out whether carbon dioxide is formed when it burns.

LABORATORY RECORD. Diagram, and full observations.

Questions:—(i) Compare the observed properties of methane and ethylene in parallel columns.

(ii) The density of ethylene is 14, and it contains $14\frac{2}{7}$ per cent. of hydrogen, the rest being carbon. What is its molecular formula?

(iii) Answer questions (iii) and (iv) of Exp. 18 for ethylene.

Exp. 20. The preparation and properties of acetylene.

Required:—As in Fig. 81; small flask, fragment of porcelain, bat's-wing burner.

DIRECTIONS. Slide a few pieces of calcium carbide into a flask and arrange as in Fig. 81.

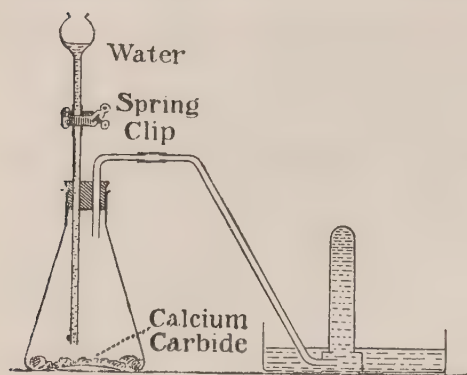


FIG. 81.

Pour some water into the funnel and let a few drops into the flask by pressing the clip.

When you think the air is displaced, collect the gas in a test-tube *until it no longer explodes* when brought to a flame. Then collect a jarful and examine its action with a

lighted taper, and notice its smell.

Remove the delivery-tube from the trough and connect it by a short piece of rubber tube to a bat's-wing burner, placed in a draught-chamber.

Let a little more water run into the flask, and ignite the gas at the burner, *after making certain that no air remains in the flask and tubes*. Put a piece of broken porcelain in the flame and **note** the deposit of carbon. Hold a flask containing cold water a little above the flame.

Note the deposit of liquid and find whether it is water. Observe the contents of the flask.

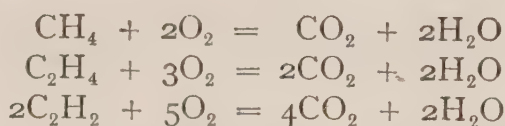
LABORATORY RECORD. Diagram; list of observed properties.

Questions:—(i) What elements have you found acetylene to contain?

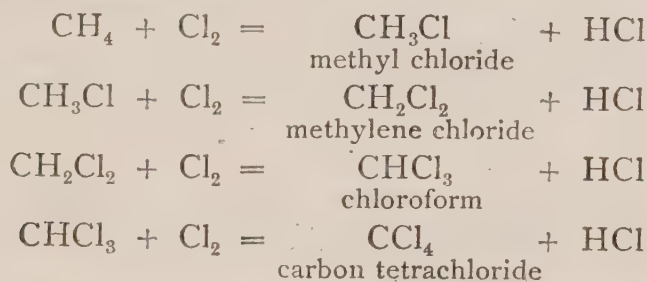
(ii) What is the white solid left in the flask?

(iii) Write an equation for the action, CaC_2 being formula of the carbide, and C_2H_2 for acetylene.

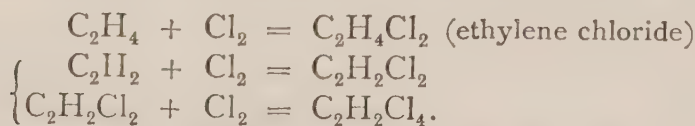
Reactions of methane, ethylene, and acetylene. By exploding known volumes of these gases with excess of oxygen in a eudiometer, and subsequent absorption of the carbon dioxide formed, their composition can be ascertained, and by determining their densities their molecular formulae can be deduced. They are: CH_4 , methane; C_2H_4 , ethylene; C_2H_2 , acetylene. On combustion in air or oxygen the actions are:—



When chlorine or bromine acts on methane at ordinary temperatures a series of *substitution* products results. With chlorine the reactions are:—



With ethylene and acetylene, *addition* products are formed:—



Corresponding bromine compounds are formed in a similar manner.

If a mixture of chlorine and any of these hydro-carbons is ignited, the only products are carbon and hydrochloric acid, thus:—



QUESTIONS ON CHAPTER XVIII.

[Assume that 1 gram-molecule of a gas occupies 22.4 l. at S.T.P.]

1. Give an account of the modes of formation and the uses of the five commercial varieties of amorphous carbon.

2. Explain what is meant by 'allotrope'. Describe the properties of the crystalline allotropes of carbon and state how the identity of their chemical nature may be established.

3. Give a full account (with diagram) of the method for determining the proportion by weight of carbon to oxygen in carbon dioxide.

4. Calculate the percentage composition of carbon dioxide from the following data:—

Wt. of boat + carbon = 8.723 g.

„ „ „ alone = 7.673 g.

Increase in wt. of absorption bulbs = 3.85 g.

5. Explain in detail a method for showing that carbon dioxide contains its own volume of oxygen. Show how to deduce its molecular formula.

6. How would you test a solid to find whether it was a carbonate? Name as many natural substances as you can which contain calcium carbonate.

7. Describe the manufacture of lime from limestone and explain the chemistry of the process.

8. Give a full account of the preparation of carbon dioxide from marble and of experiments to show its chief *physical* properties. Why is sulphuric acid not used in the preparation?

9. Describe experiments to show the action of carbon dioxide on (a) burning sulphur, (b) burning magnesium, (c) caustic potash solution.

10. Starting with carbon dioxide and sodium hydroxide, explain fully how you could make crystals of (a) sodium carbonate, (b) sodium bicarbonate. Why are these substances called 'washing soda' and 'baking soda' respectively?

11. Given solutions of magnesium nitrate and sodium carbonate, how would you prepare pure magnesium carbonate?

12. How many litres of carbon dioxide at 17° C. and 770 mm. pressure can be obtained from 150 g. of marble? What weight of hydrochloric acid solution, containing 25 per cent. of its weight of hydrogen chloride, would be required for the action?

13. What weight of calcium carbonate will yield 10 litres of carbon dioxide (a) at S.T.P., (b) at 27° C. and 740 mm. pressure?

14. What is the maximum (a) weight, (b) volume at S.T.P. of carbon dioxide that can be absorbed by 10 g. of caustic potash when dissolved in water?

15. How is the percentage weight of carbon dioxide obtainable from a carbonate determined? Give details.

16. Devise a method for finding the proportion of calcium and magnesium carbonates in a mixture of the two, being given that 100 g. of the former and 84 g. of the latter yield 44 g. of carbon dioxide, in each case, when treated with hydrochloric acid.
17. Write a complete account of the action of carbon dioxide on lime-water. Apply this to explain the chemistry of softening a temporarily hard water by (a) heat, (b) lime. Give equations.
18. Define the terms 'hard' and 'soft' in relation to water. Distinguish between temporary and permanent hardness; state and explain the action of soap on hard water. How may a 'permanently hard' water be softened?
19. Explain how it may be proved that soap is a salt of an acid composed chiefly of carbon and hydrogen. Name some acids of which the salts are soaps. How is soap made from lard?
20. Write a brief account of natural waters.
21. Explain *in detail* how you would obtain chemically pure water from muddy river water. What is the action of pure water on lead?
22. Describe the reduction of carbon dioxide by charcoal, and hence explain why a blue flame is often seen at the top of a coke fire.
23. What are 'producer gas', 'water-gas', 'Mond gas'? How are they made? Explain the chemical changes which result in the formation of these gases.
24. Give an account of the preparation of carbon monoxide from oxalic acid and describe experiments to show its chief properties.
25. Compare the properties of the two oxides of carbon, drawing up a list in tabular form.
26. How can it be shown that carbon monoxide contains half its own volume of oxygen?
27. Show how the gravimetric composition of carbon monoxide may be deduced from that of the dioxide when the volumetric composition of both is known. How is the formula CO deduced?
28. Describe the preparation and chief properties of marsh gas (methane).
29. 10 c.c. of a hydro-carbon required 30 c.c. of oxygen for its complete combustion. By absorption with potash it was found that 20 c.c. of carbon dioxide had been formed. What is the molecular formula of the hydro-carbon?
30. How is ethylene made? Compare its properties with those of methane.
31. Describe the preparation of acetylene and give a short account of its obvious properties. How can you show that it contains carbon and hydrogen?
32. What volume of air containing 21 per cent. of oxygen is required for the complete combustion of 10 l. of acetylene, both gases being at the same temperature?

CHAPTER XIX

SILICON AND SOME OF ITS COMPOUNDS

Occurrence. Silicon is one of the most abundant elements in the earth's crust, of which it forms about a quarter, and is only less plentiful than oxygen. Its oxide, silica (SiO_2), occurs as quartz or rock crystal. Sand is quartz which has been pulverized by weathering and the action of water. Flint, jasper, chalcedony, onyx, agate, carnelian, and onyx are hydrated forms of silica.

Igneous rocks, i.e. those which have been in a molten state, are composed of compounds of silica with various metallic oxides called silicates, often mixed with free silica.

Thus granite is a mixture of silica with orthoclase, a silicate of aluminium and potassium, and mica, also a silicate. A large number of rock-forming silicates is known, mostly of great complexity. A few well-known examples are augite, hornblende, asbestos (magnesium silicate), talc, and olivine.

The element silicon. Large quantities of silicon are prepared at Niagara by the passage of a very powerful current of electricity through a mixture of coke and sand. The silicon melts and can be run off, but a portion combines with carbon and forms silicon carbide (CSi), called carborundum, a substance of extraordinary hardness now much used for grinding purposes.

To prepare small quantities of silicon, sand may be heated with magnesium powder.

Exp. I. To prepare a specimen of amorphous silicon.

Required:—Pure sand or dry silica, magnesium, acids, flask, and delivery-tube.

DIRECTIONS. Weigh out 3 grams of pure sand or finely divided silica, previously dried at 120° in an oven. Mix thoroughly with 2.4 grams of dry magnesium powder and put the mixture in a dry test-tube. Hold the tube in a holder and heat gently at first, then more strongly. When the chemical action begins, stop heating until it ceases, then heat the whole mass from end to end strongly.

Let the tube cool, break it, and put the black mass into a basin. Cover with dilute hydrochloric acid and boil till all action ceases.

(Some silicon hydride is likely to come off, owing to the action of the acid on magnesium silicide, which is usually present.



Silicon hydride ignites on exposure to air and burns to silicon dioxide and water.)

Wash the mass by boiling with water and decanting into a filter funnel attached to a rapid filtration apparatus, and finally dry in an oven.

Examine the dry solid and try the action of concentrated acids upon it. Heat a small portion to redness in an open crucible.

Place the rest in a small flask fitted with a cork and delivery-tube; add sodium hydroxide solution and warm. Collect the gas which is evolved over water and test it for hydrogen.

Filter the liquid and add ammonium chloride. The precipitate is gelatinous silica.

LABORATORY RECORD. Description and observations.

Questions:—(i) Write an equation for the action of sand with magnesium.

(ii) Supposing that silicon when heated with sodium hydroxide solution gives hydrogen and sodium silicate, Na_2SiO_3 , what equation will express the action?

Silicic acid and silicates. When sodium carbonate and sand are fused together, carbon dioxide and sodium metasilicate are formed.



This silicate is made in large quantities for commercial purposes and is sold under the name of 'water-glass'.

Exp. 2. To make sodium silicate, silicic acid, and silica.

Required:—Sand, sodium carbonate, crucible, materials for dialyser, hydrochloric acid, &c.

DIRECTIONS. Mix powdered dehydrated sodium carbonate and sand in about equal bulk, and half fill a crucible with the mixture. Heat strongly until effervescence stops. When the mass is cool, boil the crucible and its contents with water in a beaker, and when all the solid except the unaltered sand has gone into solution, filter.

Divide the filtrate into two portions, (a) and (b). Add excess of ammonium hydroxide* to (a). **Note** the effect.

Prepare a *dialyser* in the following manner:—Bore a quarter inch hole in a three-quarter inch cork. Now cut out a circular piece of parchment paper of six inches diameter, and having soaked it in water till soft, tie the edges round the cork so as to make a bag, leaving a piece of loose string. Having made the filtrate (b) acid with hydrochloric acid, pour it into the parchment dialyser and hang it up in a large beaker, into which a continuous stream of water is flowing. Withdraw some of the contents of the bag after an hour and test for a chloride.

When all chloride has passed out through the parchment, a solution of colloidal† silicic acid remains in the dialyser. Test a portion of the solution for acid, and to another portion

* A solution of ammonia gas in water ; see p. 383.

† Colloids (Lat. colla, gum) are solids incapable of forming crystals or acting as electrolytes. Crystalloids are solids which can be obtained as crystals, and which in solution are electrolytes.

add ammonium hydroxide. This should cause the formation of a precipitate or jelly of silicic acid.

Wash the silicic acid, dry in an oven, and heat strongly. The residue is silica (SiO_2).

A substance in colloidal solution is called a **hydrosol**, and is unable to pass through animal or vegetable membranes as salts and electrolytes in general, called crystalloids, can do.

When a hydrosol separates from solution as a jelly it becomes a **hydrogel**.

In this experiment the crystalloid substances which passed through the parchment were hydrochloric acid and sodium chloride, whilst silicic acid (H_4SiO_4) was the colloid.

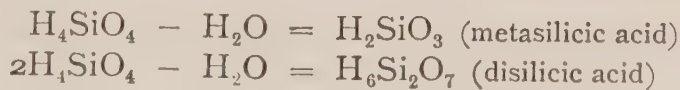


LABORATORY RECORD. Description and observations.

Questions:—(i) Write an equation for the action of heat on silicic acid.

(ii) Explain the terms: dialysis, colloid, crystalloid, hydrosol, and hydrogel.

Ortho- and metasilicic acids. Silicic acid as prepared above appears to have the composition represented by the formula H_4SiO_4 or $\text{Si}(\text{OH})_4$; this is called orthosilicic acid. Many silicates are known which do not contain the SiO_4 radical, and they may be supposed to be salts of other acids (which have not been isolated) derived from the ortho acid by loss of water, e. g. :—



Kaolin (china clay) is a hydrated orthosilicate of aluminium. Serpentine is a disilicate of magnesium, $\text{Mg}_3\text{Si}_2\text{O}_7$.

Orthosilicic acid has very feeble acidic properties, even feebler than carbonic acid. It does not form a salt with ammonium hydroxide—this substance merely causes the precipitation of the acid from its solution or from that of the sodium metasilicate.

Glass. Ordinary crown or window glass is a complex silicate of sodium and calcium mixed with excess of silica, which results from melting a mixture of sodium carbonate, limestone, and pure sand. Its *approximate* composition is shown thus:—



Soft glass, or soda glass, such as is used for some kinds of chemical apparatus, contains a smaller proportion of sand; this makes it melt more easily, and it softens enough in a Bunsen flame to allow of its being bent. Soft glass is partially soluble in water, as can be observed by boiling water in a new glass vessel and testing with neutral litmus. The dissolved sodium silicate turns it blue.

Hard glass, or Bohemian glass, is less easily melted and less soluble in water. It is made by using potassium carbonate (K_2CO_3) instead of sodium carbonate, and is used for making flasks, combustion tubes, and many other vessels used in a laboratory.

Flint glass, or lead glass, contains less sand than the others, a little soda or potash, and a large proportion of lead oxide. It is very soft, is partly dissolved by water, and attacked by acids like soda glass. It has a high specific gravity, a higher index of refraction than crown glass, and a bright lustre. It is used for making lenses, prisms, table glass and ornaments.

Coloured glass is made by adding small quantities of various metallic oxides which form coloured silicates; cobalt oxide for blue, cupric oxide or ferrous oxide for green, uranium oxide for yellow glass. Cuprous oxide and copper or gold form free metals and produce red or ruby glass. Milk glass contains bone-ash (calcium phosphate) in suspension.

Porcelain, clay, and earthenware are chiefly composed of silicates of aluminium (see p. 504).

Halogen compounds of silicon. The tetrachloride, SiCl_4 , is formed by passing chlorine over a heated mixture of silica and carbon.



It is a fuming liquid, and when its vapour is passed over heated silicon, a lower chloride is obtained.



On heating silicon in hydrogen chloride, hydrogen, SiHCl_3 (silico-chloroform) and SiCl_4 are obtained.

The tetrafluoride, SiF_4 , results from the action of hydrogen fluoride on silica, glass, and other silicates.

The relationship of carbon and silicon. These elements occur as the first and second members respectively of Group IV of the table, p. 317. They have certain distinct similarities, but they also exhibit great differences in their compounds. Both elements occur in allotropic forms. The valency of each is 4, as is seen by comparing the following molecular formulae:—



Silicon does not form an immense number of hydrogen compounds like carbon; on the other hand, it forms a very large number of complex silicates which have no analogy among the carbonates. Silicon is as notable an element in inorganic or mineral substances of Nature, as carbon is in organic substances, i.e. those derived in the process of animal and vegetable life.

QUESTIONS ON CHAPTER XIX.

1. What is the composition of agate, quartz, granite, sand, asbestos?
2. How is silicon obtained (*a*) on the large scale, (*b*) in small quantities? Describe its chief properties. What is carborundum?
3. Describe how silicic acid can be obtained, starting with sand. Explain the chemistry of the process.
4. Define the following terms, and give examples :—dialysis, crystalloid, colloid, hydrosol, hydrogel.
5. How are water-glass and window glass made? State the differences between soft, hard, and flint glass.
6. Compare the elements carbon and silicon in connexion with the periodic system.

CHAPTER XX

THE COMPOUNDS OF NITROGEN

Sources of ammonia. When coal is subjected to 'dry distillation' (see Exp. 6, p. 126) a heavy tarry liquid mixed with a lighter one is obtained. Large quantities of these liquids are produced in gas-works by cooling the gases and vapours which issue from the retorts. They are collected in a tank called the tar-pit, the tar sinking to the bottom, while the lighter liquid, called *ammoniacal liquor*, floats on the top. This is the chief source of ammonia and its derivatives.

Besides coal, many other animal and vegetable products yield ammonia on 'destructive' or 'dry' distillation; e.g. *horn*, which was largely used as a source before the introduction of coal-gas. Hence the name *spirit of hartshorn* for a solution of ammonia.

To obtain ammonia on the large scale, the ammoniacal liquor, consisting of water with ammonia and other substances in solution, is mixed with lime and heated. Ammonia gas is produced and passed into pure water, where it dissolves; the other substances are left behind. In Exp. 1, p. 289, it was observed that ammonia formed a white solid substance when brought into contact with hydrochloric acid. This substance is known as *sal-ammoniac* or, in modern nomenclature, ammonium chloride. It is made on the large scale by dissolving the ammonia gas in hydrochloric acid solution instead of water; on evaporation the solid is obtained. Similarly, if the gas be passed into sulphuric acid, *ammonium sulphate* is produced. The latter is largely used as a 'fertilizer' or artificial manure.

Exp. 1. To examine some properties of ammonium chloride.

Required:—Ignition tubes, test-tubes, ammonium chloride, silver nitrate, litmus-papers, dry lime, caustic soda.

DIRECTIONS. *A.* Describe its appearance, find whether it is soluble in water, and discover what action it has (if any) on solutions of neutral litmus and silver nitrate.

Heat a little in an ignition tube, with pieces of red and blue litmus-paper in the mouth of the tube.

Note whether (*a*) either litmus-paper is affected; (*b*) there is any smell; (*c*) water is formed; (*d*) a sublimate forms.

B. Mix some dry quicklime with about half its volume of ammonium chloride in a test-tube. Heat and **note** the same points as in *A*.

Incline the tube with its mouth upwards, and invert a wider tube over it to find whether the gas (*ammonia*) can be collected by upward displacement of air. If none is obtained, find whether it may be collected by downward displacement of air.

Invert the wide tube in a basin of water to find whether ammonia gas dissolves or not.

C. Find the effect of heating strong solutions of ammonium chloride and caustic soda in a wide test-tube.

LABORATORY RECORD. Brief description; full observations.

Questions:—(i) Does ammonium chloride contain water of crystallization?

(ii) Is any water produced in *B*?

(iii) What substances are produced by the action of hydrochloric acid on lime?

(iv) Assuming that ammonium chloride is a compound of hydrochloric acid (HCl) and ammonia, what other substances should be produced on heating it with lime (CaO)?

(v) By what tests can ammonia gas be recognized?

(vi) Is it best collected (*a*) over water, (*b*) by upward displacement, or (*c*) by downward displacement of air?

(vii) How would you make the gas on a larger scale (*a*) most economically, (*b*) most conveniently?

Exp. 2. To prepare ammonia and to examine some of its properties.

Required:—As in Exp. 1 and Fig. 82; 2 gas-jars, glass plates, platinum wire, litmus-paper, hydrochloric and sulphuric acids, taper.

Preparation. Fix an exit-tube to a wide tube, T, as in Fig. 82, but incline T slightly, making the corked end lowest.

Into T put a mixture of *dry* powdered quicklime (2 parts) and ammonium chloride (1 part).

Fix a dry inverted gas-jar over the mouth of the exit-tube.

Wrap a piece of wire gauze round T and heat the mixture gently by moving a flame to and fro along the tube.

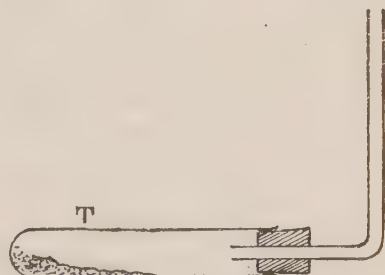


FIG. 82.

As soon as the smell of ammonia shows that the gas is escaping from the jar, remove it, closing it with a glass plate, and keeping it inverted.

As each jar is filled, use it to examine one of the *properties of the gas* as follows:—

Action with water. Put one jar mouth downwards into a basin of water and take away the glass plate. Shake a little and **note** what happens.

Put on the plate and remove the jar and its contents; smell the liquid and find its effect on red and blue litmus.

Action on acids. Put two drops of strong hydrochloric acid in a jar, close with a plate, and shake. Over this jar invert one of ammonia gas and withdraw both plates. **Note** what happens. Repeat, using sulphuric acid.

Action on a taper. Push a lighted taper up into an inverted jar of the gas. **Note** whether the gas burns or supports the combustion of a taper.

Apply a taper to the gas issuing from the exit-tube of the generator. **Note** whether the gas burns (*a*) while the lighted taper is present, (*b*) after it is removed.

Examination of the residue in the tube. Heat the tube in a draught-chamber till no more ammonia comes off. When cold, shake up the solid residue with water, and filter from excess of lime. Test a portion of the filtrate with silver nitrate solution; evaporate the remainder to dryness. Try the flame coloration.

Leave the solid (obtained by evaporation) in air for some time and **note** what happens.

LABORATORY RECORD. Diagram, brief description, observations, and *list of the properties* of ammonia.

Questions:—(i) What was formed in the action with acids? How could you verify your answer?

(ii) What solid is formed when lime and ammonium chloride are heated together? Does any of the latter volatilize unchanged?

(iii) Was your answer to question (iv) of Exp. 1 correct?

(iv) Can sulphuric acid be used to dry ammonia gas? Give a reason.

PROBLEMS (XX. 2). 1. Prepare a strong aqueous solution of ammonia, using the absorption apparatus shown in Fig. 64 (p. 289), or two wash-bottles c, d as in Fig. 65 (p. 290).

2. Find whether ammonia can be obtained by heating *ammonium sulphate* with *caustic potash*. Try the action in absence and in presence of water.

3. Find whether *calcium chloride* is a suitable agent for drying ammonia or not.

Best conditions for the preparation of dry ammonia. The previous experiments and problems will have shown that ammonia is readily produced from an ammonium salt by heating it with any of the three common alkalis. On the large scale lime is employed on account of its low cost, but if heated with ammonium chloride as in Exp. 1, in a glass vessel, the method is open to certain objections. Two solids, however well they are mixed, are not in very intimate contact, and as chemical change only occurs at such points of contact, it is difficult to obtain *all* the ammonia from the salt. Further, since ammonium compounds are volatile, the

high temperature causes the removal of a portion of the ammonium compound from the sphere of action.

These drawbacks are partially remedied by addition of water. The lime only dissolves slightly, but the ammonium salt dissolves and is kept from volatilizing. The temperature also is kept lower. Hence lime and water (i. e. milk of lime) is preferable to quicklime. This method, however, requires attention, as 'bumping' is liable to occur, especially as the water gradually evaporates.

In the laboratory, a mixture of caustic soda (or potash) with the ammonium salt and enough water to make a saturated solution when hot, is the most convenient method. This is open to none of the previous objections, but the gas is mixed with water vapour and requires to be dried. For this purpose Exp. 2 shows that sulphuric acid is impossible, because ammonia combines with it to form ammonium sulphate; calcium chloride and phosphoric oxide are also found to react with it; hence either soda-lime (formed by fusing quicklime and caustic soda) or quicklime alone is used. As a large quantity of water comes over, a relatively large amount of the drying agent will be required.

The gas may also be readily obtained by merely heating its aqueous solution without addition of any alkali.

Exp. 3. To prepare dry ammonia from a solution of an ammonium salt, and to analyse it.

Required:—Ammonium chloride, caustic soda, quicklime, copper oxide, and apparatus of Figs. 83 and 84.

DIRECTIONS. Fill one-third of a small flask, A (Fig. 83), with water. Add ammonium chloride till no more will dissolve in the cold; add a further quantity and some solid caustic soda.

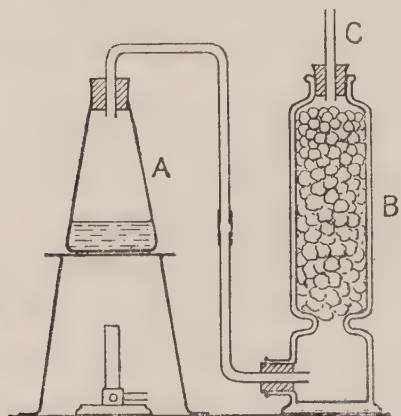


FIG. 83.

Connect the exit-tube of the flask with a wide tube, or drying tower B, containing quicklime.

Heat the flask gently over gauze.

Hold a red litmus-paper at the exit-tube, c, to find when the gas comes off.

Action on hot copper oxide. Connect c with a short combustion tube, d, packed with dried granulated copper oxide.

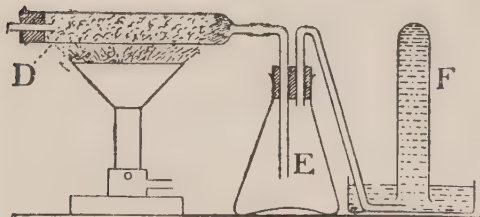


FIG. 84.

Join this to an empty flask, E, and arrange as in Fig. 84.

Heat the copper oxide for some time and then pass the dried ammonia over it. **Note** what happens in D and E, and in the inverted tube F.

Test the contents of the tube F with a lighted taper and lime-water. Identify the liquid in E.

LABORATORY RECORD. Diagrams of the *actual* apparatus; description of what was done, with observations.

Questions:—(i) What gas was found in F, and what liquid in E? What solid was left in D?

(ii) What conclusion can you draw about the composition of ammonia?

(iii) How could Exp. 3 be modified to find the gravimetric composition of ammonia, without actually weighing the gas?

* **Exp. 4. The volumetric composition of ammonia.**

Required:—Hofmann tube as in Fig. 85; rubber bands, chlorine gas, strong solution of ammonia.

The object of the experiment is to allow a known volume of chlorine to act on excess of ammonia solution and to find the volume of nitrogen obtained.

Knowing the volumetric composition of hydrogen chloride, that of ammonia can be deduced.

A tube, divided by two rubber bands into three equal parts as shown in Fig. 85, is very carefully and *completely filled* with chlorine gas by displacement of air.

A strong solution of ammonia is placed in the funnel L and the stopper pressed in.

The solution is run into the chlorine, drop by drop, by turning the tap at M.

Note the action when the tap is opened.

When no further action occurs on addition of another drop of the solution, M is closed and the liquid in L is poured out. L is rinsed with dilute sulphuric acid and then filled with water which is allowed to enter N through the tap. When the water ceases to drop, M is closed and the volume of residual gas (nitrogen) in N is noted.



FIG. 85.

LABORATORY RECORD. Description, diagram, and observations.
Questions:—(i) What is the action of hydrogen chloride on ammonia?

- (ii) What were the white fumes produced in the tube?
- (iii) Does it matter if more ammonia solution than is really required is admitted to the tube? Give a reason.
- (iv) What is the ratio of the volume of nitrogen left to the volume of chlorine taken?

* Demonstration.

Molecular formula of ammonia. From the result of Exp. 4, together with a knowledge of the volumetric composition of hydrogen chloride, the density of ammonia and nitrogen, and the atomic weight of nitrogen, the constitution of a molecule of ammonia can be deduced. Thus :—

	chlorine 1 vol.	combines with	hydrogen 1 vol.	(p. 239);
∴	3 vols.	combine with	3 vols.	
But,	chlorine 3 vols.	displace from ammonia	nitrogen 1 vol.	(Exp. 4);
∴	hydrogen 3 vols.	were united, as ammonia, to	nitrogen 1 vol.	

Again, density of nitrogen = 14 ;

∴ in ammonia, $\frac{\text{wt. of nitrogen}}{\text{wt. of hydrogen}} = \frac{14}{3}$.

Now, density of ammonia gas is 8.5 ;

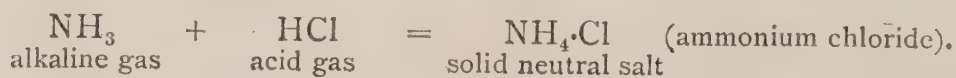
∴ M.W. of ammonia = 17 (= 14 + 3).

The A.W. of nitrogen is 14, and of hydrogen 1.

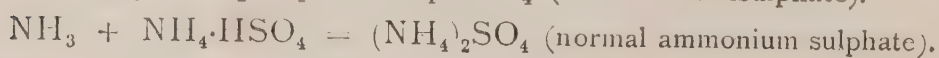
∴ ammonia contains nitrogen + hydrogen.
1 molecule 1 atom 3 atoms

Hence, NH_3 represents 1 molecule of ammonia.

The ammonium radical. It can be shown by experiment that one volume of ammonia combines with one volume of hydrogen chloride gas to form solid ammonium chloride. Hence, an equal number of molecules of each gas unite, and the simplest equation is—



The solid produced is a salt, and in many respects resembles sodium chloride (NaCl). With a dibasic acid (i. e. one containing two replaceable hydrogen atoms per molecule) two salts are obtained :—



The formation of the normal salt may also be written :—

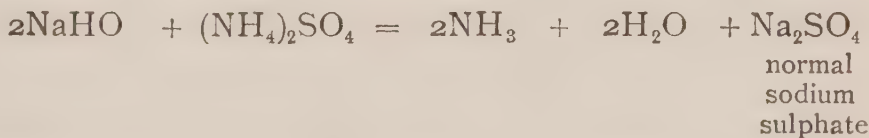
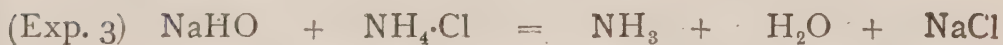
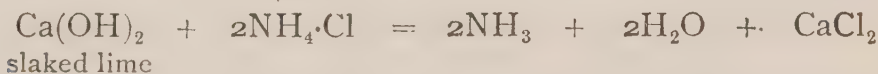
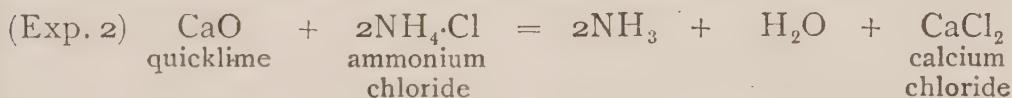


Ammonium salts all contain the radical NH_4 (ammonium), formed from the ammonia (NH_3), and one atom of hydrogen from the acid.

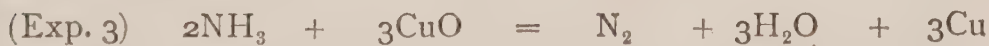
Although it consists of two non-metals, it plays the part of a metal, i.e. the ammonium radical in a molecule of ammonium chloride corresponds to the sodium atom in a molecule of sodium chloride (NaCl).

Numerous attempts have been made to isolate ammonium (NH_4), but none have succeeded, a mixture of ammonia (NH_3) and hydrogen always being obtained. Like the metals it is an electro-positive radical, but they are *simple* radicals, while ammonium is a *compound* radical.

The valency of the radical is 1, i.e. one NH_4 group replaces one atom of hydrogen, as the above equations show. The majority of ammonium salts are volatile and soluble in water. They are all decomposed by heating with an alkali, ammonia gas, a salt and water being produced, e.g. :—



Equations for the other observed reactions of ammonia are :—



Exp. 5. To compare the effect of solutions of (a) ammonia, (b) sodium hydroxide on metallic salts.

Required:—Solutions of lead nitrate, ferric chloride, sodium hydroxide and ammonia ; small basins, rapid filter.

DIRECTIONS. *A.* Fill one-third of a small basin with lead nitrate solution and add strong sodium hydroxide solution with constant stirring, till precipitation is complete.

Filter with rapid filtration apparatus, and wash the precipitate with water until no longer alkaline. Dry the solid in an air-oven at 110°C . Then heat a little in a dry tube and identify both products.

B. Repeat *A*, using ammonia solution in excess.

C. Repeat *A*, using ferric chloride and sodium hydroxide.

D. Repeat *A*, using solutions of ferric chloride and ammonia.

LABORATORY RECORD. Description ; complete observations.

Questions:—(i) What decomposition products were obtained from the precipitate in *A*?

(ii) Write equations for the two actions in *A* ; the first is one of double decomposition and the second one of simple decomposition. (Formula for lead nitrate, $\text{Pb}(\text{NO}_3)_2$.)

(iii) Is the precipitate in *B* identical with that in *A*?

(iv) What conclusion can you draw about the composition of ammonia solution?

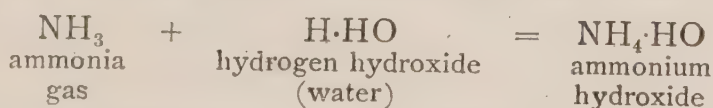
(v) Write equations for the action in *C*. (The formula for ferric chloride is FeCl_3 .)

PROBLEMS (XX. 5). 1. Investigate the action of (a) sodium hydroxide, (b) ammonia on solutions of *copper sulphate, zinc chloride*.

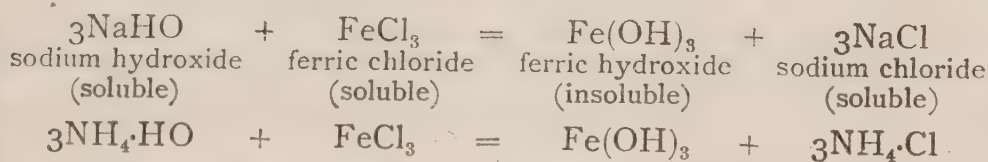
2. Find whether mercuric hydroxide is formed or not by the action of sodium hydroxide on *mercuric sulphate*.

3. Try to obtain a white oxide of tin from *stannic chloride*, and a black oxide from *stannous chloride*. In the latter case the oxide must not be heated above 100°C . in air.

Ammonium hydroxide. Exp. 5 has shown that a solution of ammonia, like solutions of sodium hydroxide (NaHO) and potassium hydroxide (KHO), precipitates insoluble hydroxides of certain metals; in fact it behaves like a soluble metallic hydroxide. For this reason a solution of ammonia is regarded not merely as a physical solution of a gas in water, but as containing *ammonium hydroxide*. The latter has never been isolated, any more than carbonic acid has been isolated, but the above evidence is considered sufficient to establish its existence in solution. Hence, when ammonia dissolves in water we may represent the chemical change thus:—



The changes which produce insoluble metallic hydroxides are cases of double decomposition, e.g. :—



Ammonia gas is peculiar in neutralizing acids with production of only *one* product—a salt. Its solution acts like a true alkali or base, producing a salt and water thus:—



The molecular formula of ammonium chloride. The symbol $\text{NH}_4\cdot\text{Cl}$ has been assumed to represent a molecule of ammonium chloride. The grounds for this assumption are:—

(a) That it is formed by the combination of ammonia gas with hydrogen chloride, no other product being obtained.

(b) That *equal* volumes of the two gases combine. Hence, by Avogadro's theory, an equal number of molecules of each gas combine to form one molecule of ammonium chloride. Since NH_3 and HCl represent molecules of ammonia and

hydrogen chloride, therefore either NH_4Cl or $\text{N}_2\text{H}_8\text{Cl}_2$ or $\text{N}_3\text{H}_{12}\text{Cl}_3$, &c., is the correct formula for the salt.

All that remains to be done is to determine whether NH_4Cl or some particular multiple is correct. This is only possible if the density of ammonium chloride vapour can be ascertained. If NH_4Cl is correct, the molecular weight is 53.5 ($=14+4+35.5$), and its vapour density must be 26.7.

Now Exp. 1 has shown that ammonium chloride is easily vaporized; hence we have an opportunity of settling the question, by finding the weight of a litre of the vapour at some convenient temperature. Experiments show that—

1 l. of ammonium chloride vapour at 350°C . and 760 mm. weighs 0.503 g.
Now 1 l. of hydrogen at 0°C . and 760 mm. weighs 0.0896 g.

\therefore 1 l. of hydrogen at 350° and 760 mm. weighs $0.0896 \times \frac{273}{623} = 0.0376$ g.

Hence, density of ammonium chloride vapour is $\frac{0.503}{0.0376} = 13.3$.

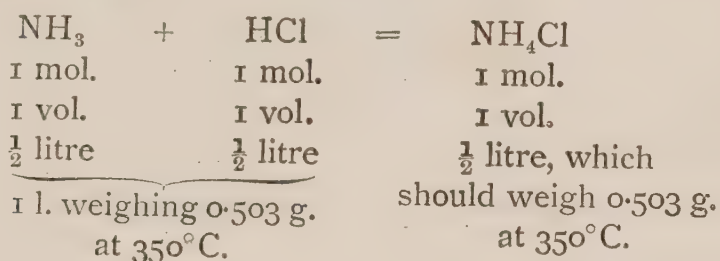
\therefore the M.W. of ammonium chloride is $13.3 \times 2 = 26.6$.

Obviously 26.6 is only half what is required by the formula NH_4Cl .

Thus, instead of settling the question between NH_4Cl , $\text{N}_2\text{H}_8\text{Cl}_2$, &c.; we find ourselves in a dilemma; either we have met an exception to Avogadro's theory or we must admit $\text{N}_{\frac{1}{2}}\text{H}_2\text{Cl}_{\frac{1}{2}}$, which is impossible on the atomic theory. For some time the former alternative was accepted, but the true cause of the apparent exception is now known.

In Exp. 1 a careful observer will have noticed that when ammonium chloride was heated, the colour of a red litmus-paper placed in the mouth of the tube changed to blue, and later on a blue paper became red. This appears to indicate that at this temperature the vapour of the salt is decomposed into ammonia and hydrogen chloride. If we can confirm this view the apparently abnormal vapour density will be explained, for we have not found the density of ammonium chloride vapour at all, but that of a mixture of equal volumes of ammonia and hydrogen chloride. The average density of

the mixture should be half the density of the compound, for 1 vol. of the acid gas + 1 vol. of ammonia should give 1 vol. of ammonium chloride vapour. That is, 2 vols. of the gaseous mixture should give 1 vol. of the compound vapour. But if we have been dealing with the mixture all the time, we never got 1 litre of ammonium chloride vapour, but $\frac{1}{2}$ a litre of ammonia, and $\frac{1}{2}$ a litre of hydrogen chloride.



If this view is correct it should be possible to separate the ammonia (density 8.5) from the acid gas (density 18.25) by diffusion; the former will diffuse into some neutral gas like air quicker than the latter. The object of the next experiment is to test this point.

Exp. 6. To find whether ammonium chloride breaks up into ammonia and hydrochloric acid gases on heating.

Required:—As in Fig. 86; hard-glass tube (2 dm. × 0.5 cm. diam.), litmus-papers, dry ammonium chloride, dry asbestos.

DIRECTIONS. Set up the apparatus shown in Fig. 86. At A put some *dried* ammonium chloride, at B a plug of well-dried asbestos. In each of the test-tubes C and D put a red and a blue litmus-paper.

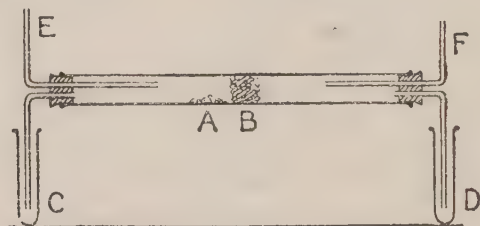


FIG. 86.

Heat A carefully for 5 minutes and gently blow down E first and then down F. **Note** any change in the litmus-papers.

LABORATORY RECORD. Diagram of actual apparatus used; full observations.

Questions:—(i) Is neutral ammonium chloride vapour obtained or not?

(ii) Account for the observed effects on each litmus-paper.

(iii) Is the abnormal vapour density of ammonium chloride accounted for or not?

Dissociation. Exp. 6 will have shown that a mixture of ammonia and hydrogen chloride is obtained by heating ammonium chloride. Hence, although these two gases combine readily at ordinary temperatures, they do not combine at higher temperatures. The change is a reversible one.



The hot gases recombine on cooling, provided that they remain in contact. To distinguish this type of chemical change from others the name **dissociation** is applied. It may be said to be a *chemical change in which the products of the decomposition of a compound by heat recombine when they are allowed to cool in contact with one another*. Recombination may also be effected by increase of pressure without cooling, a fact which is utilized in the preparation of oxygen from the air by Brin's process (p. 109).

All cases of dissociation are reversible chemical changes.

It will be remembered that calcium carbonate is decomposed at a high temperature into lime and carbon dioxide. This change is also a case of dissociation. Complete decomposition is only effected at a very high temperature, or at a lower temperature if the gaseous product of dissociation (carbon dioxide) is continually removed, so that its pressure cannot rise.

If calcium carbonate is heated to a given temperature in a closed vessel, decomposition takes place, and continues until the pressure of the carbon dioxide has reached a definite value, called the *dissociation* or *equilibrium pressure*, which is constant for this temperature. If the carbon dioxide is allowed to escape, more calcium carbonate will be decomposed until the pressure of the gas has again reached the dissociation pressure. Only by keeping the pressure of the carbon dioxide below the 'dissociation pressure' at a given temperature can complete decomposition of the calcium carbonate be effected.

Completed and incomplete reactions. In connexion with dissociation and reversible chemical changes important facts have been discovered by studying the reactions of solutions.

When two compounds are mixed in solution, if one of the products is gaseous it escapes or, if insoluble, is precipitated. In either case the reaction is *completed*.

The next experiment is to show the effect of mixing together solutions of salts which give no insoluble or gaseous product.

Exp. 7. To examine the effect of mixing saturated solutions of sodium chloride and copper sulphate.

Into three beakers, (a), (b), and (c), put respectively 1, 2, and 3 test-tubefuls of salt solution; add to each 1 test-tubeful of copper sulphate, and **note** the colour in each case.

Now fill up beaker (c) with salt solution.

Evaporate solution (a) to crystallizing point and observe the crystals under a microscope.

Questions:—(i) What is the colour of copper chloride?

(ii) What substances have been formed by mixing copper sulphate with sodium chloride?

(iii) By what means would you endeavour to cause the reaction to become as complete as possible?

In discussing the action of heat on calcium carbonate it was shown that if the carbon dioxide is allowed to accumulate at a given temperature, the change comes to an end, since for each temperature, in the presence of CaCO_3 and CaO , there is a definite pressure of carbon dioxide called the dissociation or equilibrium pressure.

The reaction $x \text{CaCO}_3 \rightarrow y \text{CaO} + y \text{CO}_2 + (x-y) \text{CaCO}_3$ only proceeds to completion when the pressure of CO_2 at a given temperature is kept below the dissociation pressure.

When two substances are mixed in solution, and when the products of their interaction are all soluble, the reaction can never be completed, though it may be caused to proceed nearer and nearer to completion by increasing the amount of one of the reagents.

Thus by adding more and more sodium chloride the reaction—

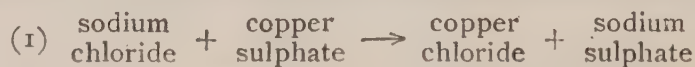


becomes more and more complete.

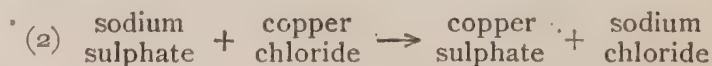
We speak of the amount of substance in a position to react as the *active mass* of that substance.

In the last experiment, since all the materials are in solution, their active masses are represented by the actual concentration of the solution.

We consider that in this reaction two opposing reactions are proceeding:



called the *direct action*;

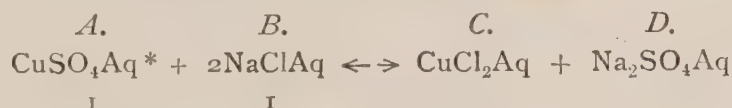


called the *reverse action*.

By increasing the concentration of sodium chloride, i.e. its active mass, we increase the rate of the direct action; and vice versa, by adding more sodium sulphate we cause the reverse action to proceed faster.

Law of Mass Action. From the study of such changes Guldberg and Waage arrived at the Law of Mass Action; *the rate of change is proportional to the active masses of the substance taking part at a constant temperature.*

Suppose the sodium chloride and copper sulphate are both present at first in equivalent quantities (see p. 253), the rate of change, i.e. the weight of sodium chloride changed to sodium sulphate in unit time, is proportional to the active masses of both the salt and copper sulphate.



Suppose 1 equivalent of A , and 1 of B present;

$$\text{Rate of change} \propto 1 \times 1,$$

$$\text{or } R = 1 \times 1 \times K.$$

This rate of change at the first instant of time is constant for this particular reaction, if the temperature does not vary, and for unit equivalent concentration is called K . Thus, $R = K$.

When after an interval of time t , x equivalents of NaCl have been transformed, the rate of change must be less, and

$$R_t = (1-x)(1-x)K = (1-x)^2 K$$

since x equivalents of CuSO_4 must also have been transformed, and also x equivalents of Na_2SO_4 and CuCl_2 are now present.

Suppose that there is equilibrium between the opposing reactions, that is to say, there is no further change in either direction, and that this has been attained when m equivalents of both NaCl and CuSO_4 have been changed to m equivalents of Na_2SO_4 and CuCl_2 .

$$\text{Then, rate at equilibrium of direct action} = (1-m)^2 K.$$

$$\text{Similarly, rate at equilibrium for reverse action} = (m)^2 K';$$

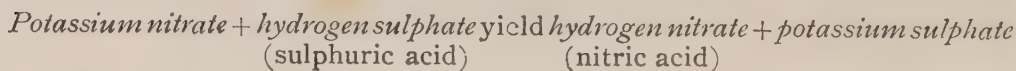
$$\therefore (1-m)^2 K = m^2 K';$$

\therefore the ratio of the rates of direct and reverse actions is

$$\frac{K}{K'} = \frac{m^2}{(1-m)^2}.$$

* Aq. (aqua) indicates that the substance is in solution.

Nitre and natural nitrates. Nitre or saltpetre was introduced into Europe about the fifth century from India. It is formed naturally by the oxidation of nitrogenous organic matter, aided by certain bacteria, resulting in the formation of nitric acid. The acid acts on the potassium salts in the soil, yielding potassium nitrate or nitre. It is used in the manufacture of gunpowder, and when treated with sulphuric acid, nitric acid is formed. Thus:—



When sulphuric acid, a non-volatile liquid, acts on salts of volatile acids, it causes the production of these acids by exchanging its hydrogen for the metal of the salt. Thus sulphuric acid and common salt cause the production of hydrochloric acid, which is a gas at S.T.P. The action with carbonates is similar.

In more recent times large deposits of sodium nitrate have been found in Chili, where it is known as *caliche* or *Chili saltpetre*. As this is much cheaper than nitre, it is used for the manufacture of nitric acid on the large scale. Its action with sulphuric acid is precisely similar to that of nitre.



*Equiv. to 1000 grams of a substance confine
with or displace 1 gr. of Hydrogen*

*Valency: No. of atoms of Hydrogen or other element
of substance.*

Exp. 8. To prepare nitric acid and to examine its action on metals, &c.

Required :—As in Fig. 87 ; concentrated sulphuric acid (commercial), nitre or caliche, copper, tin, iron, zinc, lead, test-tubes.

Preparation. Put a test-tubeful of nitre or sodium nitrate on a piece of paper. Fold the paper and slip the salt into the retort through the tubulure. Arrange the retort and receiver* as in Fig. 87.

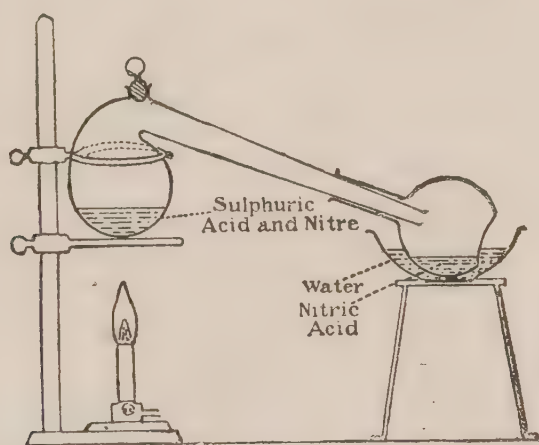


FIG. 87.

Put a thistle funnel into the tubulure of the retort and carefully pour in enough concentrated sulphuric acid to cover the solid.

Carefully remove the funnel without dropping acid from it, and wash it.

Close the tubulure with the stopper and gently heat the retort over gauze. As soon as nitric acid begins to condense in the neck of the retort, cool the receiver with cold water. Continue heating until no more liquid appears to distil.

Then remove the flame and take the receiver out of the trough, leaving the end of the retort over the water.

Precaution ;—*Nitric acid is very corrosive ; avoid dropping it on your clothes and on the bench.*

[Over.

* Or the receiver may be fixed on a ring under a water-tap.

Note the colour of the acid; and find the effect of blowing over it, and its action with litmus.

Action on metals. Place a few copper turnings in a test-tube and pour in three or four drops of the nitric acid just prepared. **Note** carefully all that happens.

Repeat, using small quantities of iron filings, granulated tin, zinc-foil, and lead-foil.

If there is no immediate action add two or three drops of water. Discover whether hydrogen is evolved or not.

Note all that happens, in each case, as carefully as possible.

Test the action of diluted nitric acid (1 : 10) on copper and tin, comparing it with that of the concentrated acid.

Leave pieces of *cork, rubber, wood, filter-paper* in a beaker containing a little strong nitric acid for some hours. Take them out, wash with water and examine them. Dry the filter-paper in an oven and then ignite it. **Note** the effects.

LABORATORY RECORD. Short description of the experiments, with list of the properties of nitric acid.

Questions:—(i) Is hydrogen produced when zinc and iron act on nitric acid, as is the case with hydrochloric and sulphuric acids?

(ii) Name any metals which only react with the acid when the water is present.

(iii) Compare the action of diluted and concentrated nitric acid on copper and tin.

PROBLEMS (XX. 8). 1. Investigate the action of diluted nitric acid (1 : 10) on *magnesium*, with special regard to the gaseous product.

2. Warm a little *sawdust* on a sand-tray and pour on it a few drops of nitric acid. Note what happens.

3. The white substance obtained by the action of nitric acid on tin is hydrated stannic oxide. On heating this, pure stannic oxide is formed. Make use of this reaction to determine the equivalent weight of tin. Use a crucible.

4. Warm a little sulphur with strong nitric acid in a flask for 10 minutes on a sand-bath placed in a draught-cupboard. Dilute well with water and test the liquid for sulphuric acid.

* **Exp. 9.** To show the action of heat on nitric acid.

Required:—As in Fig. 88 ; nitric acid, wood splinter, flask.

Connect a silica tube *c* with a thistle funnel *AB* bent as shown in Fig. 88, and drawn out at *B* so that it enters the wider silica tube. The acid to be introduced through *A* will then not touch the rubber connector.

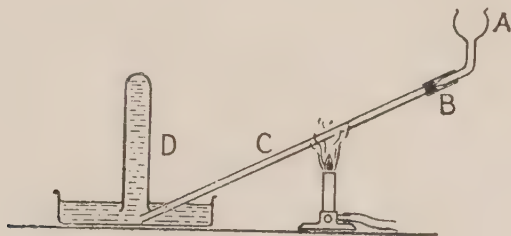


FIG. 88.

Clamp *c* at the higher end and let the lower end first dip into a *dry flask* (not as in Fig. 88).

Heat the middle of *c* strongly and pour a *few* drops of pure concentrated nitric acid into the funnel. As soon as it reaches the hot part it is decomposed, and the products pass into the flask. **Note** what happens. Identify the liquid.

Then place the mouth of *c* in a trough of water, as in Fig. 88, and decompose a little more acid. Identify the gas which collects in the tube *D*.

LABORATORY RECORD. Description, diagram, list of decomposition products.

Questions:—(i) Is nitric acid stable or unstable with regard to heat?

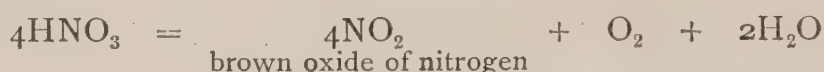
(ii) Does nitric acid contain (*a*) hydrogen, (*b*) oxygen? Quote evidence.

(iii) Is an unstable (i.e. easily decomposable) or a stable substance most likely to enter into a large number of chemical changes, that is, to be chemically active?

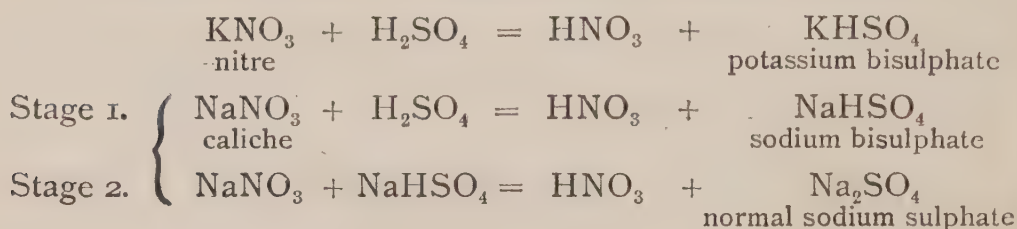
* Demonstration.

Manufacture and purification of nitric acid. On the large scale, a mixture of Chili saltpetre and sulphuric acid is heated in an iron retort, and the nitric acid vapours collected in a series of large earthenware jars standing in the open air. As was seen in Exp. 7, nitric acid is partially decomposed even during its preparation, water, oxygen, and the brown oxide of nitrogen (p. 401) being produced. The latter dissolves in the acid and discolours it. To remove the water it is redistilled, after being mixed with an equal volume of concentrated sulphuric acid. To remove the last traces of the brown gas a current of warm air is passed through. The acid then becomes colourless, but soon becomes brown again if exposed to light in a warm room.

Some reactions of nitric acid. Nitric acid is a compound of hydrogen, oxygen, and nitrogen in proportions represented by its molecular formula HNO_3 . When heated it breaks up thus:—



The equations for its preparation and manufacture are:—



Exp. 10. To prepare ammonium nitrate and to examine its properties.

Required:—Ammonia solution (sp. g. 0.88), nitric acid (sp. g. 1.5), evaporating-dish (200 c.c.), test-tubes, thermometer, sulphuric acid, copper turnings.

Preparation. Put half a test-tubeful of a saturated solution of ammonia in a large evaporating-dish and *dilute it with four times its volume* of water.

Precaution:—*The action is violent unless the substances are well diluted.*

Dilute a test-tubeful of concentrated nitric acid with four tubefuls of water and *carefully* add it to the ammonia solution until neutral. Evaporate to crystallizing point.

Properties. Put some of the crystals in a test-tube, add water and stir with a thermometer. **Note** the temperature.

Heat some in an ignition tube. **Note** whether it (*a*) takes long to melt; (*b*) contains water of crystallization; (*c*) gives off a gas which relights a glowing splinter; (*d*) leaves a residue.

Heat a little with caustic soda solution and **note** what gas is evolved. To a quarter of a tubeful of conc. sulphuric acid add an equal volume of water and cool the mixture. Into this put a little of the salt and some copper. Warm gently and **note** the result. (Keep the rest of the salt for Exp. 11.)

LABORATORY RECORD. Description of each experiment; observations.

Questions:—(i) What evidence is there that ammonium nitrate has a high latent heat of fusion?

(ii) How can (*a*) ammonia, (*b*) nitric acid, be made from ammonium nitrate?

(iii) Is ammonium nitrate explosive? Account for the flame produced in the tube.

(iv) Write an equation for the formation of ammonium nitrate.

PROBLEM (XX. 10). Prepare ammonium sulphate, diluting each substance with water as in Exp. 10. Find the action of heat and lime on it.

Exp. II. To collect and examine the gas obtained by heating ammonium nitrate.

Required:—As above and in Fig. 89; taper, charcoal, sulphur, phosphorus, gas-jars, deflagrating spoon.

DIRECTIONS. Set up a wide test-tube, or small flask, with delivery-tube as in Fig. 89.

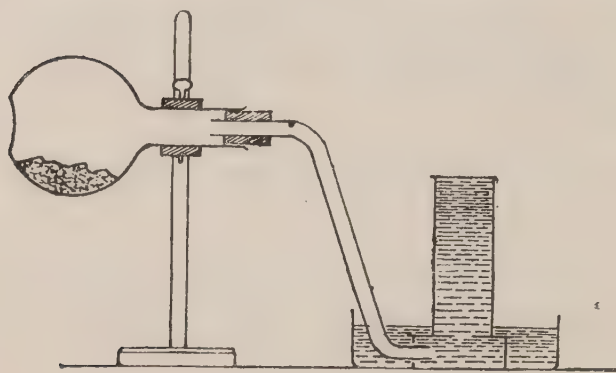


FIG. 89.

See that there is no leak, and put about 20 g. of ammonium nitrate into the vessel.

Heat gently until it is melted and a good deal of water of crystallization has been

given off. Then put the delivery-tube in the trough and collect the gas in jars, after having found that a tubeful relights a glowing splinter.

Precautions:—*Avoid heating too long; remove the delivery-tube before removing the lamp.*

Properties. **Note** the appearance and smell of the gas.

Invert a test-tubeful of the gas in a beaker of water, and shake it from time to time. **Note** whether the gas dissolves at all in water.

Find whether it supports the combustion of (a) feebly burning sulphur, (b) strongly burning sulphur, (c) burning phosphorus, (d) glowing charcoal, using a fresh jar of the gas for each substance. Determine whether oxides of these substances are produced or not.

Repeat (c) and identify the residual gas in the jar.

LABORATORY RECORD. Diagram; observations; list of properties.

Questions:—(i) Give reasons for the precautions.

(ii) Would it be better to collect the gas over warm water?

(iii) Does the gas contain (a) oxygen, (b) nitrogen? Quote evidence.

(iv) Compare the properties of this gas with those of oxygen.

PROBLEMS (XX. 11). 1. Devise a method for finding the weight of 1 litre of the dry gas. Carry it out, if approved, and calculate its density with reference to hydrogen.

2. Find what is formed when the gas is passed over *strongly* heated copper. Collect the gaseous product over water. Submit your plan for approval. Hence, deduce a plan for analysing it quantitatively.

Nitrous oxide. The gas obtained in Exp. 11 is often called 'laughing-gas', owing to the fact that, when inhaled along with air, it produces hysterical fits of laughter. In larger quantities it causes insensibility, and is used by dentists as an anaesthetic. This property was discovered by Sir Humphry Davy.

The complete investigation of the action of burning phosphorus on the gas will have shown that phosphoric oxide is formed, and that nitrogen remains in the jar. It therefore contains oxygen and nitrogen. That it is a compound of these gases, and not a mixture of them as air is, may be inferred from the fact that feebly burning sulphur is extinguished in this gas, while it continues to burn in the free oxygen of the air. Well-ignited sulphur continues to burn because enough heat is present to decompose the compound, and the combustion is continued by the liberated oxygen. Further, the composition of the gas extracted from its solution in water has the same composition as the original gas before solution. This would not be the case were it a mixture, since oxygen is more soluble than nitrogen and the extract would contain a larger proportion of the former. The very fact that it is much more soluble in cold water than either nitrogen or oxygen also supports the view that it is a compound and not a mixture. The name given to it is *nitrous oxide*.

Its *volumetric composition* may be determined by exploding one volume of hydrogen and one of nitrous oxide in a eudiometer. The only residual gas is nitrogen; this occupies one volume, i.e. the same volume as the nitrous

oxide taken. Since one volume of hydrogen has disappeared, it must have combined with *half* a volume of oxygen. Hence,

2 vols. of nitrous oxide yield 2 vols. nitrogen + 1 vol. oxygen.

It is found to have a density of 22;

∴ it has a molecular weight of 44;

i.e. 22.4 litres of it weigh 44 grams.

The eudiometer shows that 22.4 l. of it contain 22.4 l. of nitrogen, i. e. 1 gram-molecule of nitrogen, or 28 grams;

∴ 44 g. contain 28 g. nitrogen and $(44 - 28 =)$ 16 g. oxygen,

∴ 1 molecule contains 2 nitrogen atoms and 1 oxygen atom (since 14 and 16 are the atomic weights of nitrogen and oxygen respectively).

∴ the molecular formula of nitrous oxide is N_2O

Since it contains one atom of oxygen per molecule, it is known as nitrogen *monoxide*.

The equation for its formation is—



(The formation of water on decomposing ammonium nitrate may be observed by first gently heating the crystals until the water of crystallization has been driven off, and then heating the anhydrous salt in a dry tube. Water condenses on the cold parts.)

If the nitrate is overheated (as occurs when very little remains in the vessel), it breaks up explosively into other products.

Exp. 12. To collect and examine the gas from the action of nitric acid on copper. *that is*

Required:—As in Fig. 51; copper (granulated), conc. nitric acid, splinter, sulphur, phosphorus, oxygen, ferrous sulphate, 2 gas-jars, deflagrating spoon.

DIRECTIONS. Slide some granulated copper into a large flask, cover it with water, and arrange as in Fig. 51. Pour a few drops of concentrated nitric acid down the funnel from time to time as required. **Note** the action in the flask.

When the air is displaced collect the gas in jars over water.

Properties. Try its action on various substances as below, refilling the jars as required.

Note its appearance and its action on air. Determine whether (a) it is an acid, alkaline, or neutral gas; (b) it dissolves in water or not; (c) it supports the combustion of a taper, sulphur, and phosphorus; (d) it contains oxygen and nitrogen.

Mix a jar of the gas with a jarful of pure oxygen. **Note** the effect, and after the action invert one of the jars in water.

Invert a test-tubeful of the gas in a basin of ferrous sulphate solution. Shake gently and **note** the result.

Heat the black liquid and **note** the effect.

LABORATORY RECORD. Brief description; diagram; *list of properties* of the gas and other observations.

Questions:—(i) How do you account for the presence of the brown gas in the flask at first? What became of it?

(ii) What is the bluish-green liquid left in the flask?

(iii) Does the gas contain (a) oxygen, (b) nitrogen? Quote evidence.

(iv) Compare its properties with those of *nitrous oxide*.

PROBLEMS (XX. 12). 1. Obtain crystals from the residue in the flask, and find the action of heat on them. Name the substances produced.

2. Find the weight of 1 litre of the dry gas at S.T.P., and calculate its density relatively to (a) air, (b) hydrogen.

Nitric oxide. The gas employed in Exp. 12 is liable to contain small quantities of nitrous oxide and other gases, mixed with the main constituent—*nitric oxide*. It may be purified by passing the mixture into a solution of ferrous sulphate, in which nitric oxide alone dissolves. On heating the black solution the pure gas is recovered, and may be collected over water. The gas is a convenient *test for free oxygen*, since a brown colour is at once produced in presence of the latter.

As nitric oxide is less easy to decompose than nitrous oxide, it is more difficult to determine its *volumetric composition*. This may be accomplished, however, by electrically heating a spiral of iron wire in the gas contained in a straight tube standing over water. After the wire has been maintained at white heat for about 20 minutes the current is stopped, and after cooling the residual nitrogen is found to occupy half the original volume. Hence, *nitric oxide contains half its own volume of nitrogen*.

Its density is found to be 15;

∴ its molecular weight is 30.

Since 2 vols. of nitric oxide contain 1 vol. nitrogen,

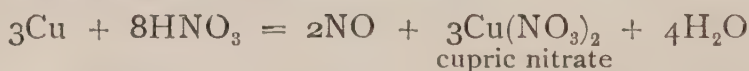
∴ 1 mol. nitric oxide contains $\frac{1}{2}$ mol. (= 1 atom) nitrogen;

∴ 30 g. nitric oxide contain 14 g. nitrogen + (30 - 14) = 16 g. oxygen;

∴ 1 mol. „ „ contains 1 atom „ + 1 atom oxygen.

Hence, NO represents a molecule of nitric oxide.

The equation for its formation is—



Tests for nitrates. (1) The action of heat on the solid (see p. 405).

(2) Heated with concentrated sulphuric acid and copper, brown fumes of nitrogen peroxide are formed.

(3) *The black-ring test.* Dilute some concentrated sulphuric acid with an equal volume of water and cool it. Pour this on the solid suspected to be a nitrate and then pour on the top a solution of ferrous sulphate and shake slightly. If the substance is a nitrate, a black ring of $2\text{FeSO}_4 \cdot \text{NO}$ will appear at the junction of the liquids.

Exp. 13. To prepare and examine the brown oxide of nitrogen.

Required:—As in Fig. 90; 3 jars, taper, phosphorus.

DIRECTIONS. Fill about a quarter of a hard-glass tube with powdered lead nitrate previously dried at 110°C .

Connect this with two test-tubes standing in a beaker or jar containing ice and salt, as in Fig. 90.

See that the whole is air-tight, and heat the powder gently as long as brown fumes come off.

Test the gas issuing from the second test-tube with a glowing splinter.

When the action in the hard tube is over, remove the flame and examine the contents of the test-tubes.

Find the effect of warming one of them by holding it in your hand, or by placing it in hot water. Fill three jars with the gas from the test-tubes by downward displacement. Invert one in water, and **note** the result, and test the liquid which enters the jar with litmus-papers. Find whether the gas supports the combustion of a taper and phosphorus. Examine and identify the coloured residue in the hard tube.

LABORATORY RECORD. Brief description; diagram; *list of properties* of the liquid and gas.

Questions:—(i) What three products are formed by heating lead nitrate ($\text{Pb}(\text{NO}_3)_2$)? Write an equation.

(ii) In what other way has the brown gas been obtained?

(iii) Does the brown gas contain (a) oxygen, (b) nitrogen? Quote evidence.

(iv) Compare the properties of the brown gas with those of nitrous and nitric oxides.

PROBLEM (XX. 13). Prepare crystalline nitrate of *mercury* by dissolving the metal in nitric acid. Carefully investigate the action of heat on the crystals.

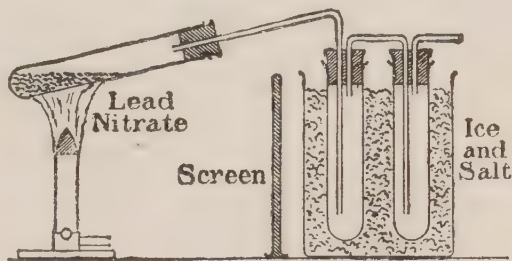


FIG. 90.

Nitrogen peroxide. Since nitric oxide combines with oxygen to produce the brown oxide, the name peroxide is given to the latter to indicate that it contains a greater proportion of oxygen than the former.

The relative density of the peroxide at 150°C . is 23 ($H = 1$), therefore its molecular weight is 46.

It can be shown by experiment that—

2 vols. nitric oxide + 1 vol. oxygen yield 2 vols. peroxide.

Now, 2 vols. nitric oxide contain 1 vol. of oxygen (p. 400),

\therefore 2 vols. of peroxide contain 2 vols. of oxygen;

\therefore 46 g. of peroxide contain 32 g. of oxygen + $(46 - 32 =)$ 14 g. of nitrogen,

or 1 mol. of peroxide contains 2 atoms of oxygen + 1 atom of nitrogen.

\therefore the molecular formula of the peroxide at 150°C . is NO_2

At lower temperatures its density (compared with hydrogen at the same temperature) is greater than 23. To account for this, it is assumed that on cooling some NO_2 molecules combine to form the more complex molecule N_2O_4 , called *nitrogen tetroxide*.

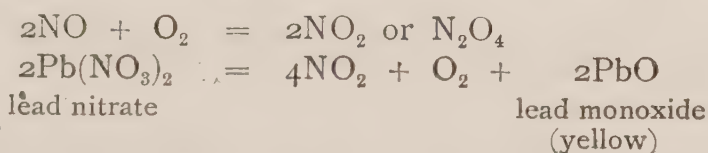
Dissociation of nitrogen tetroxide. The investigation of the vapour density of this substance shows that it undergoes dissociation (see p. 386). Apparently this begins while the substance is in the liquid state, since it undergoes changes of colour as the temperature rises. At low temperatures it is a colourless crystalline solid, melting at -9°C . into a colourless liquid. On raising the temperature the colour changes to pale yellow, becoming orange yellow at about 15° . It boils at 22° , giving a reddish-brown vapour, and this becomes darker, until at 140° it is almost opaque. On cooling, the same changes occur in the reverse order.

At 27°	the vapour density is	38,	corresponding to	20 %	NO_2
" 60°	"	"	30	"	"
" 100°	"	"	24	"	"
" 140°	"	"	23	"	"

The density corresponding to N_2O_4 is 46, while that for NO_2 is 23. Hence, as a vapour, it never consists wholly of N_2O_4 molecules, but is assumed to do so in the liquid state when it is colourless.

Reactions of nitrogen peroxide. (The name nitrogen dioxide is occasionally given to the brown gas, but this is not usual; nitric oxide was also formerly known as the dioxide. Since confusion is likely to arise from the term 'dioxide', it is generally avoided in both cases.)

The equations for its formation are—



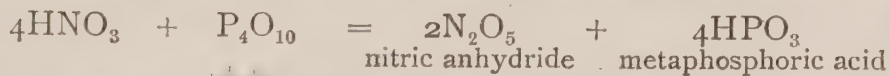
All other nitrates decompose on heating like lead nitrate, except those of potassium, sodium, and ammonium.

When it dissolves in cold water, a mixture of nitric and nitrous acids is formed, thus:—



Two **other oxides of nitrogen** are known, corresponding to the formulae N_2O_3 and N_2O_5 . The former is called nitrogen trioxide, and the latter nitrogen pentoxide or nitric anhydride.

The *pentoxide* is made by distilling pure nitric acid with phosphoric oxide, which acts as a dehydrating agent thus:—



The pentoxide is a solid, and on addition of water nitric acid is re-formed:—



The preparation of nitrogen from its compounds. It was mentioned on p. 114 that nitrogen from the air contains small quantities of several other gases, and consequently is not pure. From a study of the properties of nitrogen it is plain that it does not readily combine with other elements.

When, however, such compounds are formed it is reasonable to expect them to be unstable and to give up their nitrogen readily. This is in fact the case.

Preliminary Questions. 1. How was nitrogen obtained from ammonia gas?

2. What happens to copper when it is heated in a current of air?

3. What would you expect to happen if a mixture of air and ammonia was passed over it? Express by equations, if possible.

4. How can nitrogen be obtained from nitrous and nitric oxides?

5. Describe the obvious properties of the solid residue left after nitre is heated.

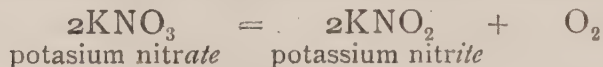
Exp. 14. To prepare ammonium nitrite and to obtain nitrogen from it.

Required:—Nitre, crucible, brick, lead, knitting needle, ammonium chloride, flask with singly-bored cork and delivery-tube.

DIRECTIONS. *A.* Melt about 10 g. of nitre in a crucible, add about 20 g. of lead-foil gradually and stir with a knitting needle until no more of it is oxidized. Pour out the hot liquid on to a brick or fire-clay slab. Boil with water, filter, and evaporate the filtrate to dryness.

To a small portion of the residue add a little cold dilute sulphuric acid. **Note** the effect and compare it with the action of the acid on nitre.

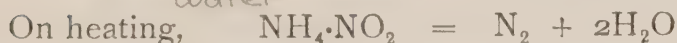
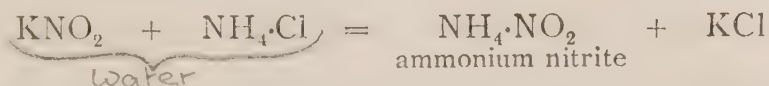
This residue is called *potassium nitrite*—the potassium salt of nitrous acid (HNO_2). It is obtained, though more slowly, by heating the nitrate alone:—



B. Put the remainder of the nitrite (or use a quarter of a stick of ready-made nitrite) in a small flask with about 5 grams of ammonium chloride, and add enough water to dissolve them. Heat the flask, having a delivery-tube attached, and collect any gas given off over water. Test the gas with a taper and lime-water.

The mixture made above results in the formation of

ammonium nitrite and potassium chloride, both of which remain in solution.



LABORATORY RECORD. Description; diagram; observations.

Questions:—(i) Does the nitrogen come from the nitre or ammonium chloride, or from both?

(ii) What is the equation for the action of heat on ammonium nitrate?

(iii) How may a nitrite be distinguished from a nitrate?

PROBLEM (XX. 14). Prepare nitrogen by passing air from a reversed aspirator through a wash-bottle of ammonia solution and through a tube of hot copper. Collect over water as usual. [This is Harcourt's method for obtaining a continuous supply of nitrogen. The bulk of it comes from the air and a little from the ammonia. It is not, of course, chemically pure nitrogen.]

Action of heat on nitrates—preparation of metallic oxides. The usual result of heating a nitrate is its decomposition into the *metallic oxide*, *nitrogen peroxide*, and *oxygen*. The action on lead nitrate (p. 403) is typical. Copper nitrate acts similarly:—



If the metallic oxide is unstable when hot, the metal itself may be formed. This is the case with the nitrates of mercury and silver:—



The nitrates of sodium and potassium are peculiar in yielding a nitrite and oxygen. Thus:—



Ammonium nitrate is quite exceptional in yielding nitrous oxide and water:—



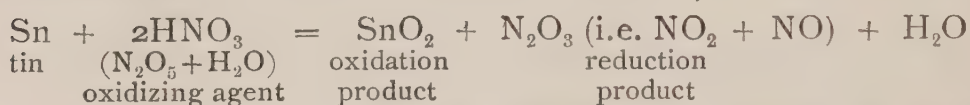
Metallic oxides may often be conveniently prepared from

a metal by treating it with nitric acid until no more brown fumes are evolved. On evaporating the nitrate to dryness and igniting the solid residue the metallic oxide remains.

Oxidizing power of nitric acid. When nitric acid acts on tin, a white residue is left of hydrated stannic oxide; on heating this, stannic oxide is formed. This substance is straw-yellow when hot, and white when cold.

Evidently nitric acid has oxidized tin to tin oxide; the acid itself being reduced to nitrogen peroxide and water.

The presence of brown fumes is always a sign that nitric acid has been causing oxidation. The action may be represented thus:—



Here nitric acid, which we may regard as nitrogen pentoxide and water, gives up oxygen to the tin and is reduced to the trioxide and water. The trioxide being unstable yields $\text{NO}_2 + \text{NO}$.

Nearly all the actions of nitric acid on metals, non-metals, and compounds are oxidizing actions. Copper (p. 399) is oxidized to copper nitrate; lead to lead nitrate, &c.; phosphorus to phosphoric acid (phosphoric *oxide* and water); carbon to carbon dioxide.

With certain organic substances it forms what are called *nitro-compounds*, or compounds containing the NO_2 radical. Thus cotton-wool (cellulose), when dipped in the concentrated acid, washed and dried, appears scarcely changed in appearance, but it is much heavier. This substance is gun-cotton, and explodes violently when detonated, though small quantities burn quietly in air.

With glycerine three $-\text{NO}_2$ groups are introduced, forming a yellow oily liquid—trinitro-glycerine. This, when absorbed by a soft earthy solid, forms a paste known as dynamite.

Lyddite is made from nitric acid and carbolic acid.

Nitric acid is used in the manufacture of all high explosives.

QUESTIONS ON CHAPTER XX.

1. Explain how ammonia can be made, starting with coal.
2. Describe, in detail, one good laboratory method for preparing ammonia gas. Give the equation for the action.
3. Calculate the amount of lime or other material necessary to extract the maximum quantity of ammonia from 2000 g. of ammonium chloride.
4. How can *dry* ammonia gas be shown to contain nitrogen and hydrogen?
5. Name four common desiccating agents, stating which can and which cannot be used to dry ammonia, and why.
6. Describe the chief physical and chemical properties of ammonia gas, briefly indicating the means of showing them experimentally. Give equations for the chemical changes.
7. Explain in detail why the formula NH_3 is taken to represent a molecule of ammonia.
8. Why is an aqueous solution of ammonia gas considered to contain ammonium hydroxide?
9. What is meant by the statement, 'Ammonium is a positive compound radical'?

10. What do the following symbols mean exactly?—



Find the volume of the gaseous product in litres, of the liquid in c.c., and the weight of the solid in grams, when 100 g. of copper oxide are used.

11. Give an account of the dissociation of ammonium chloride, and its bearing on the formula $\text{NH}_4\cdot\text{Cl}$.

12. State the law of mass action and describe an experiment in illustration of it.

13. Describe the preparation of nitric acid in the laboratory. How can it be purified from dissolved brown fumes?

14. Give as complete an account as possible of the action of nitric acid on metals.

15. What is the action of heat on nitric acid? Is a 'strong' acid necessarily a very difficult substance to decompose?

16. Describe the effect of nitric acid on some common substances, such as wood, paper, cotton-wool, &c.

17. What weight of nitric acid can be obtained when 150 g. of sulphuric acid react with 100 g. of nitre?

18. How is ammonium nitrate made? What gas does it yield on heating? Describe the preparation and properties of the gas.

19. What volume of nitrous oxide (*a*) at S.T.P., (*b*) at 27°C . and 780 mm. pressure, can be obtained from 150 g. of ammonium nitrate?

20. What weight of ammonium nitrate is required to yield 20 l. of nitrous oxide (a) at S.T.P., (b) at 27° C. and 780 mm. pressure?
21. Give a full account of the preparation of nitric oxide.
22. Tabulate the properties of nitrous oxide, nitric oxide, and oxygen (in parallel columns) to show their differences.
23. Explain fully how the molecular formulae for nitrous and nitric oxides can be established.
24. How can liquid nitrogen tetroxide be made? Mention its obvious properties, and state the evidence for concluding that it dissociates on heating.
25. How is potassium nitrite made? Compare its properties with those of the nitrate.
26. Compare the action of heat on ammonium nitrite with that on ammonium nitrate.
27. How may a *continuous* supply of nitrogen be easily obtained?
28. Give an account of the oxidizing action of nitric acid in four cases, with equations.
29. What weight of nitric acid can be got from one ton of (a) nitre, (b) caliche?
30. Explain how nitric oxide could be used to determine the percentage volume of oxygen in air. Give details.
31. What volume of nitric oxide at S.T.P. will just combine with (a) 2.5 l. of oxygen at 17° C. and 740 mm., (b) the oxygen in 10 l. of air at S.T.P.? [Assume air to contain 21 per cent. of oxygen by volume.]
32. If 150 c.c. of ammonia gas are confined over mercury and 80 c.c. of hydrochloric acid gas are admitted, what will be the composition and volume of the residual gas?
33. Calculate the percentage composition of the five oxides of nitrogen from their formulae.
34. Calculate the volumes of oxygen and nitrogen obtainable from 10 l. of each of the gaseous oxides of nitrogen.
35. Starting with metallic copper, tin, and nitric acid, explain how cupric and stannic oxides can be obtained.
36. In the dissociation of calcium carbonate



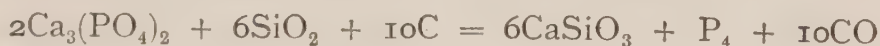
taking K and K' as the rates at which the direct and reverse actions proceed, and r , r' and p as the active masses of the carbonate, lime and carbon dioxide respectively, make out an equation showing how these quantities are related when the system is in equilibrium.

CHAPTER XXI

PHOSPHORUS AND ITS CHIEF COMPOUNDS

The element phosphorus. Phosphorus is an important constituent of animal tissues, bones containing a large proportion of calcium phosphate; moreover, plants will only produce seed if sufficient phosphorus is supplied from the soil.

Manufacture. The element is prepared from calcium phosphate by reduction, in presence of carbon and sand, in a special form of electric furnace. The phosphorus goes off as vapour and is condensed in water, whilst carbon monoxide escapes and the calcium silicate which remains in the retort is run off from time to time in a molten state.



Properties. Prepared thus, phosphorus is a white wax-like solid melting at 44°C . Ordinary phosphorus is luminous in the dark, oxidation to one or other of the oxides taking place, whilst ozone is simultaneously produced (p. 449). In pure oxygen at air pressure phosphorus is not luminous, but if the pressure is reduced it becomes luminous. Volatile oils such as turpentine, which destroy ozone, prevent luminosity.

Phosphorus is soluble in carbon disulphide, and if the solution is poured on blotting-paper, as soon as the solvent has evaporated oxidation becomes so rapid that the paper quickly inflames.

Ordinary phosphorus combines with the halogens with great evolution of heat.

Allotropic forms. When heated in absence of air to about 250°C . it changes to a red variety or allotrope with a considerable evolution of heat. This change occurs at lower

temperatures if a trace of iodine be present. The commercial process consists in heating yellow phosphorus in iron bottles having a narrow tube passing through the stopper. The oxygen in the air present unites with a little phosphorus, leaving an atmosphere of nitrogen. When the change is as complete as possible, the mass is extracted with carbon disulphide to dissolve any traces of unaltered yellow phosphorus.

The yellow colour of ordinary phosphorus is due to its surface having changed to the red variety owing to long exposure to light. The principal differences in properties are given in the following table:—

ORDINARY PHOSPHORUS.	RED PHOSPHORUS.
White, semi-transparent, crystalline solid, gradually yellow by light.	Dark red, opaque, crystalline solid, unaffected by light.
Luminous in the dark.	Non-luminous.
Sp. g. 1.8.	Sp. g. 2.1.
Melts at 44° C.	Does not melt, vaporizes above 250° C.
Very poisonous.	Non-poisonous.
Very soluble in carbon disulphide.	Insoluble.
Inflames in air at 35°-45° C.	Does not inflame below 240° C.

Phosphorus was formerly used in making lucifer matches—a certain amount of yellow phosphorus being contained in the head of ordinary matches. In safety matches the head contains potassium chlorate, antimony sulphide, and a little powdered glass, while the preparation on the box contains red phosphorus and antimony sulphide. The use of yellow phosphorus is now prohibited.

Hydrides of phosphorus. When magnesium nitride is treated with water, magnesium oxide and ammonia are formed. Similarly, metallic phosphides, such as of calcium or magnesium, give phosphorus hydride by treatment with water.

Exp. I. To observe the formation of phosphorus hydride.

Fill two-thirds of a very small hard-glass tube with dried calcium phosphate; push a strip of magnesium ribbon to the bottom of the tube and heat strongly. (The magnesium takes the oxygen from the phosphate, leaving the phosphide, Ca_3P_2 .) Now add a few drops of water to the contents of the tube and note the result—the gas produced is phosphorus hydride, PH_3 .

Usual method of preparation. Ordinary phosphorus is heated with water and potassium or barium hydroxide in a flask, air having first been displaced from the apparatus by coal-gas. The reaction is expressed by the equation:—



The gas is led off by a delivery-tube and collected over water.

Properties. Phosphorus trihydride or phosphine is a colourless gas having a smell like rotten fish, and is rather soluble in water, but its chemical properties vary according to its method of preparation. As prepared above, it is spontaneously inflammable. By passing the gas through a cooled U-tube, a liquid condenses, and the escaping gas has not the power of inflaming on contact with air. The liquid has a vapour density corresponding to the formula P_2H_4 , and causes the spontaneous ignition of the gas on exposure to air.

Phosphine is easily decomposed by heat, and has strong reducing power owing to the readiness with which it parts with hydrogen.

Phosphine (PH_3), like ammonia (NH_3), forms unstable compounds with the halogen hydrides. The most stable of these compounds is PH_4I , called phosphonium iodide.

Chlorides of phosphorus. The two chlorides, PCl_3 and PCl_5 , are both formed by direct combination of the elements, the former using excess of phosphorus and the latter when chlorine is in excess. The apparatus shown in Fig. 91 is suitable for their preparation.

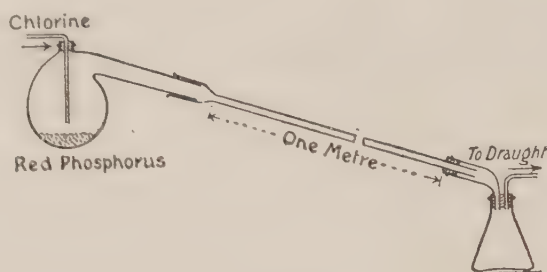
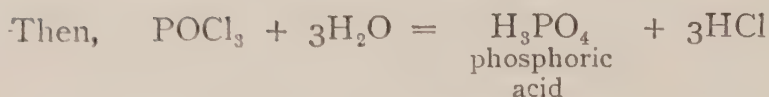
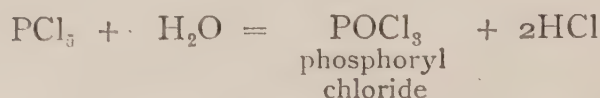
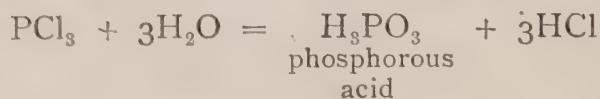


FIG. 91.

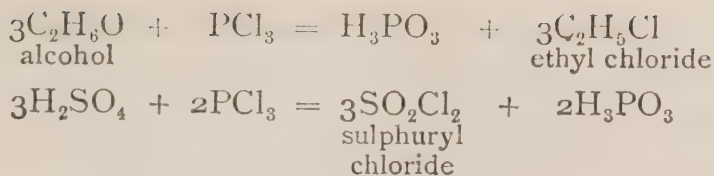
The trichloride is purified and freed from the pentachloride by distilling from red phosphorus; it is then a colourless fuming liquid which boils at 76°C .

By passing chlorine into the trichloride, the pentachloride, a pale yellow solid, is formed. When heated, phosphorus pentachloride vaporizes without melting, and gives an abnormal vapour density, and from its greenish-yellow colour the vapour must contain free chlorine. Thus, $\text{PCl}_5 \leftrightarrow \text{PCl}_3 + \text{Cl}_2$ (see dissociation of ammonium chloride, p. 386).

Both chlorides are very ready to react with other substances; thus with water a violent reaction takes place.



Any substance containing the hydroxyl (OH) group, behaves in a similar manner, so that PCl_3 or PCl_5 may be used as means for detecting hydroxyl. Thus alcohol ($\text{C}_2\text{H}_6\text{O}$) and sulphuric acid (H_2SO_4) both react with PCl_3 .



Alcohol must therefore contain one hydroxyl group and be $\text{C}_2\text{H}_5\text{OH}$, whilst two OH groups are present in the sulphuric acid molecule, whose formula may accordingly be written $(\text{HO})_2\text{SO}_2$.

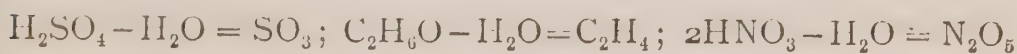
Other halogen derivatives. Two bromides, very similar to the chlorides, are known, and two iodides, PI_3 and P_2I_4 , may be prepared by the action of iodine on a solution of phosphorus in carbon bisulphide. A fluoride, PF_5 , is also known and exists as a stable gas at the ordinary temperature.

The oxides of phosphorus. Three oxides are known, P_4O_{10} , P_4O_6 , and P_2O_4 .

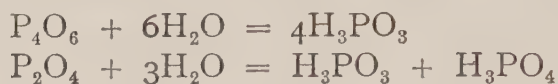
Phosphorus pentoxide. This has already been prepared in an impure state in Exp. 5, p. 86. To obtain the pure substance, free from trioxide, the crude oxide must be distilled in a current of dried oxygen. It is then obtained as a pure white crystalline solid, more volatile at 210°C . than at any other temperature, and giving a vapour density corresponding to the formula P_4O_{10} . It is extremely deliquescent, forming one or other of the phosphoric acids according to the amount of water present. Thus—



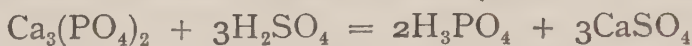
On account of its absorbent powers for water, it is largely used for the removal of the last traces of water from gases. It also acts chemically on many compounds containing the elements of water, such as sulphuric acid, which yields sulphur trioxide; alcohol ($\text{C}_2\text{H}_5\text{O}$), which gives ethylene (C_2H_4), by loss of water; and nitric acid, which gives nitrogen pentoxide.



Phosphorus trioxide, P_4O_6 , and the *tetroxide*, P_2O_4 , are both difficult to prepare. They are formed by the incomplete combustion of phosphorus. Both are colourless volatile solids whose vapour densities correspond to the above formulae. They react with water thus:—

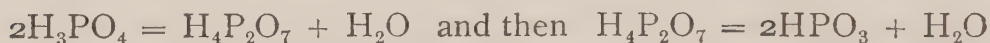


Phosphoric acid, H_3PO_4 . Phosphorus pentoxide is the anhydride of this acid. It is made by the action of sulphuric acid on bone ash, which is mainly calcium phosphate, $Ca_3(PO_4)_2$, the soluble phosphoric acid being separated from the very slightly soluble calcium sulphate by decantation.



The liquid is evaporated until it is syrupy. When sufficient water has been removed the liquid will crystallize on cooling; it is then known as 'glacial' phosphoric acid.

The orthophosphoric acid loses water on heating, pyrophosphoric acid, $H_4P_2O_7$, being first formed, and at a higher temperature, the meta-acid HPO_3 .



Phosphoric acid is tribasic, and can form three salts with sodium, Na_3PO_4 , Na_2HPO_4 , and NaH_2PO_4 . Disodium hydrogen phosphate is the common sodium phosphate in use in the laboratory as a reagent. Na_3PO_4 and Na_2HPO_4 are alkaline in solution, whilst the dihydrogen salt gives an acid solution.

Detection of a phosphate in solution. When a phosphate in nitric acid solution is allowed to stand after addition of a solution of ammonium molybdate, $(NH_4)_3MoO_4$, a bright yellow compound of complex composition is deposited.

The nitrogen group of elements. Referring to the table of the periodic system of the elements on p. 317, it will be seen that the typical elements of the group are nitrogen and phosphorus, followed by arsenic, antimony, and bismuth.

This group shows a well-marked gradation of physical and chemical properties with increasing atomic weight. Thus nitrogen and phosphorus are fairly typical non-metals, arsenic and antimony lie on the border, and bismuth has the most strongly marked metallic character of all.

The hydrides, NH_3 , PH_3 , AsH_3 , and SbH_3 , are in the order of decreasing stability and decreasingly basic character. Bismuth forms no hydride.

The stability of the chlorides towards water increases with increasing atomic weight, and the acidity of the oxides decreases. Following is a table showing some of the chief compounds of these elements.

Props. of Element.	N	P	As	Sb	Bi
A.W.	14	31	75	120	207
Molecule of gas or vapour	N ₂	P ₄	As ₄	—	—
Number of forms	One form only	Two forms: red and yellow	Three forms	One form	One form
Hydrides	$\left. \begin{array}{l} \text{NH}_3 \\ \text{N}_2\text{H}_4 \\ \text{N}_3\text{H} \end{array} \right\} \begin{array}{l} \text{basic} \\ \\ \text{acid} \end{array}$	Stability PH ₃ weak base P ₂ H ₄ (liquid) Acidity	decreasing AsH ₃ not basic	SbH ₃ not basic	None
Oxides	$\left. \begin{array}{l} \text{N}_2\text{O} \\ \text{NO} \\ \text{N}_2\text{O}_6 \\ \text{N}_2\text{O}_4 \\ \text{N}_2\text{O}_5 \end{array} \right\} \begin{array}{l} \text{salts known} \\ \\ \\ \\ \end{array}$	— — P ₄ O ₆ P ₂ O ₄ P ₄ O ₁₀ H ₃ PO ₃ HPO ₃ H ₁ P ₂ O ₇ H ₃ PO ₄	decreasing — — As ₄ O ₆ — As ₂ O ₅ H ₃ AsO ₃ HAsO ₃ H ₄ As ₂ O ₇ H ₃ AsO ₄	Sb ₄ O ₆ Sb ₂ O ₄ Sb ₂ O ₅ Similar to arsenic but acids very weak	Bi ₂ O ₃ Bi ₂ O ₅ acidic HBiO ₃
Acids	(HNO ₂) salts known HNO ₃	Stability towards water increasing PCl ₃ PCl ₅ None	water increasing AsCl ₃ None	SbCl ₃ Forms salts decomposed by water	BiCl ₃ Salts fairly stable towards water
Chlorides	NCl ₃ Explosive None				
Salts					

QUESTIONS ON CHAPTER XXI.

1. Describe how you would prove the presence of phosphorus in a mineral phosphate.
2. State fully the reasons for regarding phosphorus as a non-metal.
3. What would you expect to result from the action of concentrated nitric acid on red phosphorus? Make out an equation for the action.
4. How are red and yellow phosphorus made? Compare their properties and devise a method for showing that the red variety contains nothing but the element phosphorus.
5. Describe the preparation and properties of the two chlorides of phosphorus.
6. By what means is the hydroxyl radical detected in compounds?
7. Give an account of the preparation and properties of phosphine.
8. Referring to the table on p. 317, you will find a gap between the elements antimony and bismuth; write a short account of what you suppose the character of this element and its compounds would be if it were known.
9. Explain and illustrate by examples the meaning of the expression, *orthophosphoric acid is tribasic*. What salts would you expect to obtain by the action of sodium hydroxide with pyrophosphoric acid?
10. Describe the method you would adopt in order to obtain the three sodium salts of orthophosphoric acid.
11. Knowing that silver phosphate (Ag_3PO_4) is insoluble in water, what substances would be formed by the addition of a solution of silver nitrate to solutions of the three orthophosphates of sodium?

CHAPTER XXII

SULPHUR AND ITS CHIEF COMPOUNDS

Preliminary Questions.

1. State the obvious properties of sulphur.
2. What changes in appearance have you noticed when melted sulphur is heated?
3. How would you separate sulphur from admixture with rock or stone on a large scale?
4. What substance is formed when sulphur burns in air or oxygen? How is it recognized? What is formed when this substance dissolves in water?
5. What substances are formed when sulphur is heated with (a) iron, (b) copper? Describe their properties.
6. Name as many natural substances as you can, which contain sulphur.
7. Describe how sulphurous acid can be oxidized to sulphuric acid.

Extraction and refining of sulphur. Advantage is taken of the readiness with which the element melts to separate it from the rock and earth with which it is found mixed in Sicily and other volcanic countries.

Extraction. The sulphur-rock is stacked loosely in kilns of brick having a sloping floor. By means of burning wood some of the sulphur is ignited, and the heat thus generated causes the main bulk of the sulphur to melt and run down on to the floor. From there it flows down the slope into rough moulds. Naturally small particles of stone float along with it and remain mixed with the crude sulphur. In this way about two-thirds of the sulphur is extracted from the rock, the remainder being used up as fuel.

Refining. To refine this product it is distilled in an iron retort and the vapour is condensed in cold brick chambers as shown in Fig. 92.

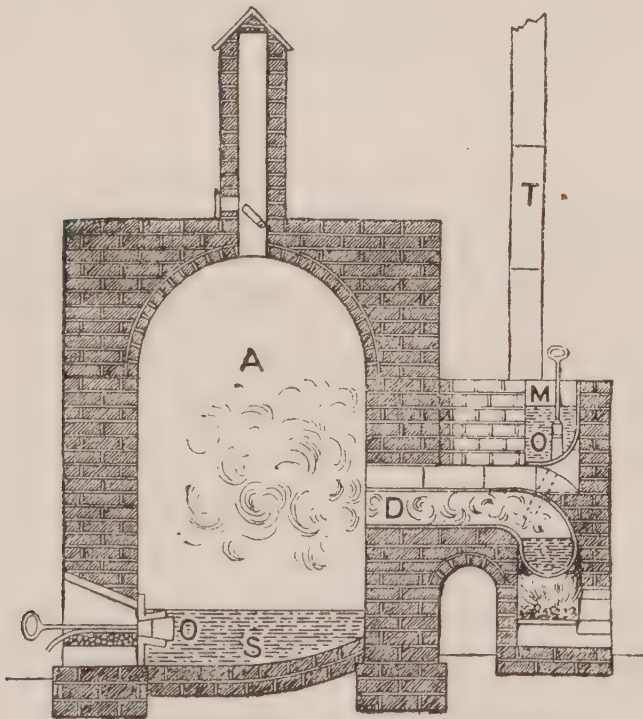


FIG. 92.

A, cold chamber. o, plug blocking exit. S, molten refined sulphur. D, exit from retort. T, furnace chimney. M, crude sulphur. o, inlet to retort.

The rough impure sulphur is melted and run into the retort; here it is boiled, and the vapour passes into the cold chamber, where it condenses in the form of a yellow powder, known as *Flowers of Sulphur*. After a time the walls of the chamber become hot, and subsequent vapours are only condensed to a liquid which collects on the floor. When enough has collected, a plug is removed, and the liquid is run out into cylindrical moulds, in which it solidifies. Sticks of sulphur made in this way are sold as *Roll Sulphur*. The particles of stone and other non-volatile impurities remain in the retort or in the melting-pot.

In order to purify it still further, it is either redistilled or dissolved in carbon disulphide and obtained from the solution by evaporation.

Test for free sulphur. Sulphur combines very readily with silver to form a black sulphide. If a minute particle of sulphur be heated on a silver coin, a black stain is produced. This forms a convenient test for the element.

Exp. 1. To examine crystals of sulphur obtained (a) from a solution, (b) by slowly cooling molten sulphur.

Required:—Sulphur, carbon disulphide, beaker, small flask, funnel, small fireclay crucible, tripod, glass rod, basin, tongs, lens, melting-point apparatus (p. 57), olive oil.

DIRECTIONS. *A.* Put about 5 g. of powdered roll sulphur into a small flask.

Add half a test-tubeful of carbon disulphide and shake.

Precaution:—*No flame must be burning on the bench during this experiment.*

Filter the solution and collect the clear liquid in a beaker.

Set it aside in a draught-cupboard until crystals have formed. (Whilst waiting, proceed with *B.*)

Pour off the clear liquid from the crystals and put them on filter-paper to drain. Examine them with a lens, and **note** their shape; put them in a dry test-tube and keep for *C*. They are specimens of **rhombic sulphur**—also called *octohedral*, or *α* sulphur.

B. Fill three-quarters of a fireclay crucible with powdered sulphur, and heat it gently on a tripod, with constant stirring. When the sulphur has all melted, allow the crucible to cool, watching it all the time. As soon as a crust forms, quickly pierce a hole in it with a glass rod, and, holding the crucible with tongs, pour out the liquid contents into a basin of water. When the crucible is cold, break away the crust from the sulphur and examine the mass below.

Note the appearance and shape of the crystals, which are specimens of **monoclinic sulphur**—sometimes called *prismatic* sulphur, or *β* sulphur.

Proceed to *C* at once, for these crystals will not keep long.

C. Put small fragments of the crystals from *A* and *B** into separate melting-point tubes. Attach them by means of rubber bands to the bulb of a thermometer. (See Fig. 20, p. 57.)

Clamp the thermometer with its bulb in a beaker containing olive oil, and heat *gently*, whilst constantly stirring, until the first sign of melting occurs. **Record** the temperature, and continue to heat the bath until the sulphur in both tubes has melted.

D. Keep some of the monoclinic crystals for a week and then re-examine them, **noting** colour, melting-point, and crystalline form when gently broken.

LABORATORY RECORD. List of observed properties of each variety; sketches of crystals; record of their melting-points.

* The monoclinic crystals must have been prepared quite recently.

Exp. 2. To observe the changes which occur when sulphur is heated to its boiling-point and then suddenly cooled.

Required:—60 c.c. flask, beaker, test-tube holder, flowers of sulphur, carbon disulphide.*

DIRECTIONS. *A.* Fill a beaker with water and place it on the bench beside you. Half fill a small flask * with sulphur, fix a test-tube holder on to the neck, and *gently* heat it over gauze. When completely melted, heat more strongly and **note** the changes in colour and fluidity.

B. When the sulphur is boiling vigorously, pour it into the beaker of water. **Note** what happens to the residue as it slowly cools in the flask.

Take the solid from the beaker and examine it; it is called **plastic sulphur**, or γ sulphur.

C. Find whether plastic sulphur is soluble or insoluble in carbon disulphide.

D. Perform the test for free sulphur mentioned on p. 420.

LABORATORY RECORD. Short description; complete observations. For Fair Notes give, in addition, a complete summary of the properties of the three varieties of sulphur.

Questions:—(i) What differences do you note between sulphur obtained by slow and rapid cooling of the melted substance?

(ii) What is the colour of the vapour from boiling sulphur?

(iii) Why is the sulphur obtained in *B* called 'plastic sulphur'?

(iv) Is plastic sulphur soluble in carbon disulphide?

(v) Do you consider the change by which plastic sulphur is formed a chemical or a physical change? Give reasons.

PROBLEM (XXII. 2). Devise a suitable means for comparing the densities of roll sulphur and plastic sulphur. If your method is approved, carry it out.

* Preferably one previously used for this experiment.

The allotropic forms and phases of sulphur. The foregoing experiments show that sulphur can exist in several different forms, viz.:—two crystalline varieties, rhombic and monoclinic sulphur, and a non-crystalline plastic form. In addition, sulphur may exist as a liquid and as a gas.

The solid varieties differ widely in their physical properties, but since equal weights of all three give the same weight of sulphuric acid when heated with nitric acid, it is certain that they all consist of the same element. They are therefore allotropic forms of sulphur.

Now when rhombic and monoclinic sulphur are heated, both melt to the same liquid, but if the liquid from either is slowly cooled, only one kind of crystal is obtained, namely, the *monoclinic* form, which melts at 119°C .

If, however, monoclinic crystals are kept at the ordinary temperature, it will be noticed that they become opaque and brittle, owing to a spontaneous change into a mass of minute rhombic crystals. Moreover, this change from the monoclinic to the rhombic form will always eventually take place unless the monoclinic crystals are kept above 96°C .; above this temperature monoclinic sulphur is stable, and rhombic sulphur will be slowly transformed into the monoclinic variety. This temperature is called the *transition point* for these two varieties of sulphur.

Since rhombic sulphur melts at 114°C . and the monoclinic form at 119°C ., we may regard these temperatures as transition points for rhombic and liquid sulphur, and for monoclinic and liquid states respectively.

The different forms, or *phases*, all consist of the same substance, but each phase is capable of permanent existence only within a definite range of temperature for a given pressure.

The phases of sulphur are as follows:—

Solid (a) Rhombic, stable below 96°C .

(β) Monoclinic, „ above 96°C . and below 119°C .

(γ) Plastic, unstable at all temperatures.

Liquid sulphur, stable above the melting-point of rhombic and below the boiling-point.

Gas, or vapour of sulphur, stable at and above the boiling-point (448°C.), when the pressure is 760 mm.

Alteration of pressure causes variation in the range of temperature within which a given phase is stable. Thus, 448° is the lowest temperature at which the gas phase is stable when the pressure is 760 mm.; at 780 mm. it would not be stable unless the temperature were increased.

Other elements, besides sulphur, are also capable of existing in several solid phases, notably phosphorus and carbon, the former of these occurring as red and yellow phosphorus and the latter in the forms of diamond, graphite, and lamp-black. These varieties differ in physical properties but not in chemical composition.

It has been found to be a general rule that the form of an element having the greatest density is the most stable.

The following table shows some physical properties of the three solid varieties of sulphur :—

	α sulphur.	β sulphur.	γ sulphur.
Colour . . .	Bright yellow.	Amber yellow.	Amber yellow.
Sp. g.	2.05.	1.98.	1.95.
Tenacity . . .	Brittle.	Brittle.	Plastic, tough.
Crystalline form . . .	Rhombic octohedra.	Monoclinic prisms.	Non-crystalline or amorphous.
Melting-point .	114°C.	119°C.	Indefinite.
Solubility in carbon disulphide . . .	Soluble.	Soluble.	Insoluble.

Peculiarities of fluid sulphur. Previous experiments will have shown that ordinary sulphur on melting at 114°C. is a pale yellow mobile liquid. On further heating it becomes

dark red and more viscous, until between 220° – 250° C. it cannot be poured out of the vessel. Above this temperature it becomes more and more mobile, though still dark in colour, up to 444° , when it boils. On sudden cooling when above 260° , plastic sulphur is formed.* The density of its vapour at 500° and 760 mm. pressure is about 96, corresponding to a molecular formula of S_6 . At lower pressures (compared with hydrogen under the same conditions) the density corresponds to a formula S_8 . Between 500° and 900° C. it expands at a greater rate than Charles's Law enunciates, and at the latter temperature its density is 32, corresponding to S_2 . At higher temperatures no further dissociation occurs.

Exp. 3. To show the effect of hydrogen on heated sulphur.

Required:—Hydrogen generator; as in Fig. 93; solution of copper chloride.

DIRECTIONS. Set up the apparatus as shown in Fig. 93 (preferably in a draught-chamber). Attach a hydrogen generator to the open end of the bulb-tube and put a *little* water in the flask, arranging so that the end of the right-angled tube dips beneath the surface.

Pass a current of hydrogen through the apparatus *until all air has been expelled*, and **note** whether the gas which escapes has any smell.

Now heat the sulphur until it boils in the bulb. Again **note** the smell. A gas called **sulphuretted hydrogen** or hydrogen sulphide has been formed.

Pour a few drops of copper chloride solution into the flask and **note** the effect. [Over.

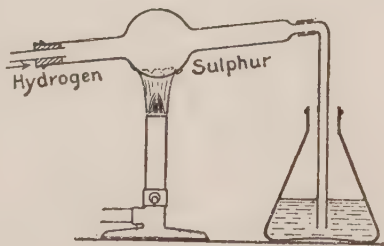


FIG. 93.

* The viscous liquid consists of two forms, one (λ) stable at lower and the other (μ) at higher temperatures. Sudden cooling prevents rapid transformation of μ to λ , and plastic sulphur—a mixture of the two—results.

LABORATORY RECORD. Diagram of apparatus ; observations.

Question :—What do you suppose is formed when hydrogen sulphide is mixed with a solution of copper chloride ?

Ferrous sulphide is formed when iron filings are heated with sulphur (p. 150). By the action of hydrochloric acid on this substance the iron is displaced from the sulphide and goes into solution as ferrous chloride, the sulphur combining with the hydrogen of the acid to form hydrogen sulphide.

Exp. 4. To prepare and examine the properties of sulphuretted hydrogen (usual laboratory method).

Required :—As in Fig. 75, p. 337 ; taper, 2 gas-jars, cover-plates, solutions of copper chloride, ferrous sulphate, chromic acid, sodium hydroxide.

Preparation. Set up the apparatus shown in Fig. 75 in a draught-chamber. Carefully slide a few pieces of ferrous sulphide into the flask, and pour diluted hydrochloric acid through the funnel until the sulphide is nearly covered. Collect the gas by downward displacement of air.

Let the action proceed until a piece of filter-paper, moistened with a solution of copper chloride and held over the mouth of the gas-jar, is rapidly blackened.

Remove and cover the jar, and replace it by another* half full of water. Obtain a strong solution of the gas for use in *B*.

N.B.—When finished, fill the generating flask with water, and pour it down a sink, if possible, in the draught-chamber. For subsequent experiments use a Kipp generator.

Properties. *A.* Put a lighted taper into a jar of hydrogen sulphide. **Note** whether it burns or supports combustion.

B. Divide the solution into three portions, *X*, *Y*, *Z*. Test one with moistened red and blue litmus-papers.

* Or use two wash-bottles each half filled with water.

Add a solution of copper chloride to *X* until the smell of hydrogen sulphide is no longer noticeable. Filter, and test the filtrate with neutral litmus solution.

Into *Y* pour a solution of ferrous sulphate ; if it still smells, add more, then test with litmus.

If no precipitate is obtained, neutralize the acid by the addition of a few drops of sodium hydroxide solution.

To the contents of *Z* add a little chromic acid solution together with a few drops of sulphuric acid. **Note** the change in colour and the precipitate. Heat the solution to boiling-point, collect, wash and identify the minute precipitate. [If the solution of hydrogen sulphide is weak, bubble the gas through the chromic acid solution for 2 or 3 minutes.]

LABORATORY RECORD. Diagram, short description, and observations in *A* and *B*.

Questions :—(i) Is hydrogen sulphide heavier or lighter than air?

Give evidence.

(ii) Why is the gas unable to support the combustion of a taper?

(iii) What is formed when the gas burns in a jar? What difference, if any, would be noticeable if it burned at a jet in air?

(iv) What is the black solid formed when the solution of the gas is mixed with copper chloride solution? What has become of the chloride radical?

(v) Explain why no ferrous sulphide was formed on the addition of ferrous sulphate to the solution of the gas ; explain the effect of adding sodium hydroxide.

(vi) Compare the action of hydrogen sulphide on chromic acid with that of nascent hydrogen (p. 220). Is the former a reducing agent?

PROBLEMS (XXII. 4). 1. Arrange 7 test-tubes in a stand, and fill one-third of each with hydrogen sulphide solution. Add to each tube, in the order given, one of the following solutions:—*zinc sulphate, lead nitrate, tin chloride, magnesium chloride, sodium chloride, antimony chloride*; and note whether a precipitate is formed or not.

If not, add a few drops of *ammonium hydroxide* and note any

[Over.

change. If a precipitate now forms, filter, wash, dry, and find whether the solid is a sulphide by heating in a J-tube of hard glass.

(The tube should have a short limb and a long one. Put the solid at the bend and heat it. The long tube acts as a chimney and causes a current of air to come over the solid. If the solid is a sulphide, sulphur dioxide will be obtained, and may be recognized by its odour.)

2. Add a few drops of *nitric acid* to a saturated solution of hydrogen sulphide in water. Explain the result.

3. Find what substances are formed when powdered *iron pyrites* is heated (a) alone, (b) in a current of air.

4. Investigate the differences between the actions of *ferrous sulphide* and *iron pyrites* when heated in air and when treated with acids.

5. Find the effect of exposing an aqueous solution of hydrogen sulphide to light in a well-corked flask. Devise some means of determining whether the presence of atmospheric oxygen is concerned with the result.

*** Exp. 5.** To ascertain the volume of hydrogen obtainable from a given volume of hydrogen sulphide.

Required:—Hydrogen sulphide generator, copper or tin-foil, glass tube as in Fig. 94 A (30 cm. long, 1 cm. diam.), basin of mercury.

DIRECTIONS. A. Draw out one end of a tube (Fig. 94 A) to a capillary opening, and when cool slip in strips of copper or tin-foil to extend along a third of its length.

Draw out the wide end also to a capillary and attach to the generator.



FIG. 94 A.

Pass the gas through the tube until it escapes freely. When full, quickly seal it at the exit by holding the point in a Bunsen flame. Immediately disconnect the other end and seal off at the constriction, being careful to avoid heating the tube at any other point.

* Demonstration.

B. When the tube is cold, carefully heat the metal as strongly as can be done without softening the glass.

When cool, put one end in a basin of mercury and break off the extreme point with tongs. **Note** whether bubbles escape, or whether mercury rises in the tube.

Try to prove that the residual gas is hydrogen.

LABORATORY RECORD. Description; observations; diagram.

Questions:—(i) What is formed when copper or tin are heated in hydrogen sulphide?

(ii) Why is it important to avoid heating the wide portion of the tube whilst sealing it?

(iii) What gas was left in the tube?

(iv) Is the volume of residual gas greater, less, or equal to that present before it was heated with the metal?

Molecular formula of hydrogen sulphide. Exp. 5 will have shown that (a) the gas left in the tube was hydrogen, (b) the volume of hydrogen is the same as that of the hydrogen sulphide, or, in other words, hydrogen sulphide contains its own volume of hydrogen.

Hydrogen sulphide
1 vol. yields hydrogen
1 vol. (Exp. 5);

∴ 1 mol. contains 1 mol. (Avogadro's theory):

∴ H_2S_x represents 1 mol. of hydrogen sulphide since H_2 represents 1 mol. of hydrogen.

The density of hydrogen sulphide is 17;

∴ M.W. „ „ „ „ 34;

∴ wt. of sulphur in 1 mol. of the sulphide is $34 - 2 = 32$ units.

But 32 is the A.W. of sulphur;

∴ 1 mol. hydrogen sulphide contains 1 atom of sulphur;

∴ $x = 1$ and H_2S represents a molecule of hydrogen sulphide.

Molecular formula of sulphur dioxide. By burning sulphur in a known volume of oxygen (as was done in Exp. 5, p. 331, for carbon) it can be shown that sulphur dioxide contains its own volume of oxygen. Thus,

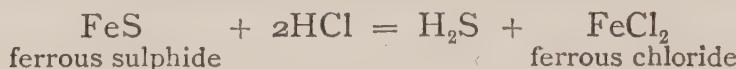
Sulphide dioxide contains oxygen;
 1 vol. 1 vol. ;
 \therefore 1 mol. 1 mol.
 \therefore S_xO_2 is molecular formula, since O_2 is molecular formula.
 The density of sulphur dioxide is 32 ;
 \therefore M.W. " " " " 64 ;
 But M.W. of oxygen is 32 ;
 \therefore wt. of sulphur in 1 mol. of sulphur dioxide is $64 - 32 = 32$ units.
 But 32 is A.W. of sulphur ;
 \therefore $x = 1$, and SO_2 represents a molecule of sulphur dioxide.

Equations for the reactions of hydrogen sulphide.
 Having established the molecular formula, we can symbolize the actions involving hydrogen sulphide.

Preparation from its elements (Exp. 3):—

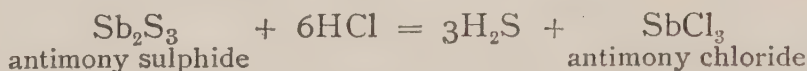


Preparation from sulphides (Exp. 4):—



Since commercial ferrous sulphide is liable to contain free iron, a certain amount of free hydrogen may be mixed with hydrogen sulphide prepared in this way.

The pure gas is obtained by heating antimony sulphide in a flask with hydrochloric acid:—



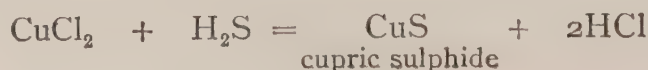
Combustion in air. (a) If air supply is limited, as when it burns in a gas-jar:—



(b) If burnt at a narrow jet, when there is plenty of air:—

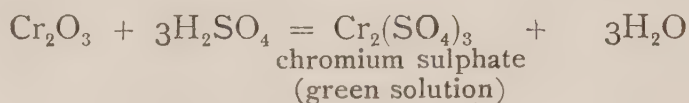
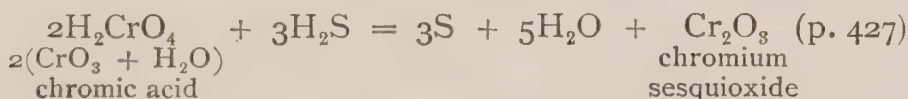


Action on solutions of metallic salts. Exp. 4 showed that a solution of copper chloride lost its colour, and that a black precipitate (copper sulphide, CuS), and an acid (HCl) were formed:—



In the case of ferrous sulphate and the salts of several other metals, no precipitate is obtained until an alkali is added, because their sulphides, though insoluble in water, dissolve in acids. As an acid is produced by the reaction, the alkali is necessary to neutralize it. In the case of a third class of metals (e. g. potassium, calcium, sodium, &c.), the sulphides are soluble in water. Hence their salts yield no precipitate with hydrogen sulphide even in alkaline solution.

The reducing action of hydrogen sulphide is apparent by its action on chromic or nitric acids. It reduces the former to the green oxide (Cr_2O_3), which dissolves in sulphuric acid, if present, producing green chromium sulphate. Sulphur is usually precipitated when hydrogen sulphide reduces, the liberated hydrogen being the real reducing agent.



Hydrogen sulphide is a feeble acid, as its action on litmus shows; it is sometimes called *sulphydric acid*. Its salts are called *sulphides*, and are usually made by double decomposition.

Sulphur dioxide and sulphurous acid. When sulphur burns in air, oxygen or sulphur dioxide is formed, according to the equation:—



When this gas is dissolved in water, sulphurous acid is formed:—



This acid, like carbonic acid (H_2CO_3), only exists in solution; attempts to free it from excess of water have failed.

Exp. 9, p. 127, showed that when sulphurous acid was warmed with mercuric oxide, the latter lost oxygen, and

sulphuric acid was formed. Hence sulphuric acid is an oxidation product of sulphurous acid.



Since H_2SO_3 may be regarded as $\text{SO}_2 + \text{H}_2\text{O}$, H_2SO_4 may be considered as $\text{SO}_3 + \text{H}_2\text{O}$; i. e. sulphuric acid is formed from water and a higher oxide of sulphur, viz. sulphur trioxide.

Exp. 6. To prepare sulphur dioxide by reducing sulphuric acid with copper (usual laboratory method).

Required:—As in Fig. 94 B; copper turnings, sulphuric acid (commercial), 2 gas-jars, taper, nitric acid, magnesium, infusion of rose leaves, solutions of chlorine, sulphuretted hydrogen, and nitrates of silver and barium.

Preparation. Use the apparatus shown in Fig. 94 B.

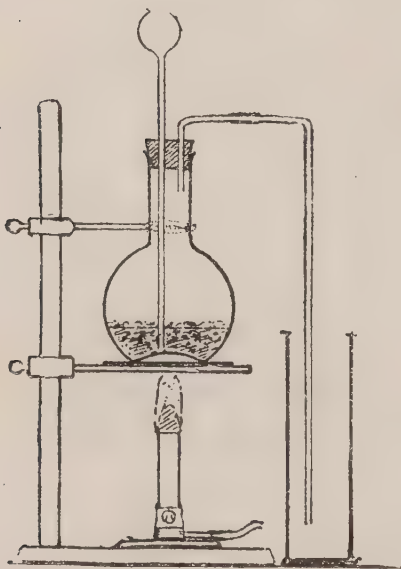


FIG. 94 B.

Cover the bottom of the flask with copper-turnings, and, having pushed the lower end of the funnel low down into the flask, add concentrated sulphuric acid to form a layer about 4 cm. deep.

Heat gently until effervescence occurs; then remove the lamp. Collect the gas in jars by downward displacement of air; test with a lighted taper to find when the jar is full.

Examine the gas in one jar, as below, while another is filling.

Then place the exit-tube in a 500 c.c. flask containing 100 c.c. of distilled water. When filled with gas, loosely cork and shake, so as to obtain a solution.

Finally, heat the generating flask in a draught-chamber until no further action occurs; allow it to cool and keep it.

Properties. (a) To the first jar add a few drops of nitric acid and **note** the result. Then add a solution of barium chloride and find whether the precipitate is soluble or insoluble in hydrochloric acid.

(b) In another hold burning magnesium ribbon. **Note** the effect. Examine the residue and find whether it is completely soluble in diluted sulphuric acid.

(c) Pour a few drops of infusion of rose leaves into another jar of the gas. Shake and **note** the effect. Divide the liquid into two portions; to one add diluted sulphuric acid, to the other a diluted alkali. **Note** the effect on the colour.

(d) To a small quantity of a solution of the gas add an equal volume of sulphuretted hydrogen solution. Identify the precipitate.

(e) Find whether the solution reduces chromic acid solution or not. (Use *very little* chromic acid.)

(f) Add a *few drops* of chlorine water to a little of the sulphur dioxide solution. Divide the liquid into two portions. Test one for a sulphate and the other for a chloride.

Examination of the residue in the flask. When all action is over and the flask is cold, add enough water to cover the residue, and warm over gauze.

Filter into a basin, evaporate to the crystallizing point; collect, dry, and identify the crystals.

N.B.—Keep the apparatus for Problem I, below.

LABORATORY RECORD. Observations on the preparation, properties, and residue. Diagrams.

Questions:—(i) If copper can reduce sulphuric acid to sulphurous acid, what solid product do you expect to form? What further action would this solid undergo in presence of excess of sulphuric acid?

(ii) What was the colour of the crystals obtained from the residue? Why was the colour not observed during the preparation?

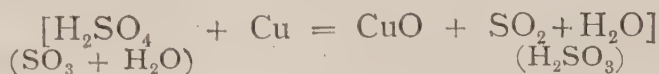
[Over.

- (iii) Write an equation for the action in (a). Name the oxidation product and the reduction product.
- (iv) Write an equation for the action in (d), on the supposition that water is one product.
- (v) The action in (e) is one of oxidation. Where does the oxygen come from? Write an equation.
- (vi) What properties of sulphur dioxide are most suitable to distinguish it from other gases?

PROBLEMS (XXII. 6). 1. Prepare *liquid sulphur dioxide* by attaching the tube from the generator to the condensing apparatus shown in Fig. 90. Let the exit-tube from the latter dip into a test-tube containing *mercury*, so as to increase the pressure slightly.

2. Investigate the action of *sulphur*, *gas-carbon*, and *mercury* on hot concentrated sulphuric acid.

Theory of the reactions of sulphur dioxide. *The action of copper on sulphuric acid* may be regarded as one of reduction. One atom of copper may be supposed to combine with one atom of oxygen from one molecule of sulphuric acid (H_2SO_4), yielding 1 mol. each of copper oxide (CuO), sulphur dioxide (SO_2), and water (H_2O).



The basic oxide cannot exist in presence of excess of sulphuric acid, but reacts with it to form a salt (copper sulphate).

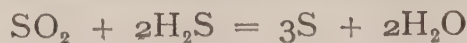


The complete action is represented thus:—



Since there is insufficient water to form the blue hydrated copper sulphate, the white anhydrous substance is obtained. This is obscured by a small amount of black cuprous sulphide, which is the result of a secondary reaction.

The *action of sulphur dioxide on sulphuretted hydrogen* in presence of water may be expressed as follows:—



Sulphur is supposed to be formed in volcanic regions by the actions of these two gases in presence of steam.

Bleaching action. Sulphur dioxide will bleach certain vegetable colours, and is used commercially to decolorize sponges, straw, flannel, &c., which would be damaged by chlorine.

The bleaching action of moist sulphur dioxide appears to be due to reduction and not to oxidation. Thus :—



The sulphurous acid takes oxygen from the water and liberates nascent hydrogen, which reacts with the colouring matter. Hence moist sulphur dioxide is a *reducing agent*.

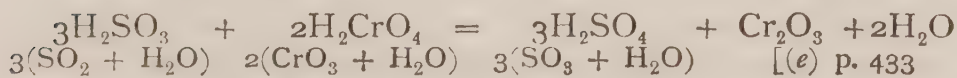
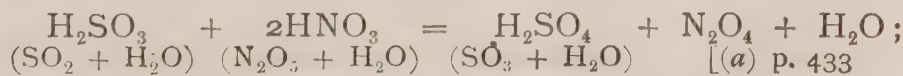
The bleaching effect is not always permanent, the original colour often reappearing on addition of an acid or an alkali. Sponges and flannel become brown in presence of soap, owing to the excess of alkali in the latter.

Oxidation of sulphur dioxide. When materials have been bleached by chlorine, some of the gas adheres tenaciously to the bleached product. Sulphur dioxide is used to remove the chlorine, and on this account is termed an 'anti-chlor'. The action is :—



The reaction takes place only in presence of water, and the two acid products are easily removed by rinsing. This reaction affords another example of the *oxidizing power of moist chlorine*. Sulphurous acid is oxidized to sulphuric acid by the oxygen liberated from water through the agency of chlorine.

Nitric acid and chromic acid and many other oxidizing agents act in a similar way to moist chlorine, e.g. :—



Cr_2O_3 , being a basic oxide, at once reacts with the sulphuric acid to form a salt and water :—



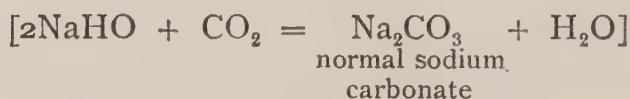
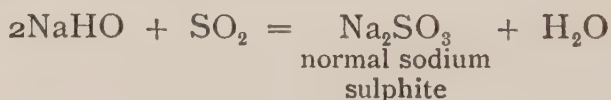
Hence the complete equation is :—



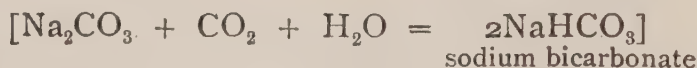
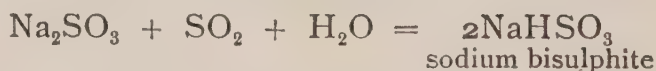
The gas is also used as a germicide and disinfectant, having the power of killing most germs or bacteria.

Sulphur dioxide is easily liquefied by cooling it with a mixture of ice and salt. The gas should first be dried by bubbling it through concentrated sulphuric acid.

Sulphites. When sulphur dioxide acts on excess of an alkali solution, a *normal* sulphite is obtained. The action is similar to that of carbon dioxide :—



When the gases are in excess, the bisulphite or bicarbonate is produced, thus :—



The action of heat on solutions of these causes the re-formation of the normal salts :—

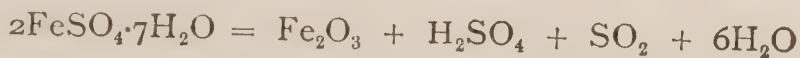


When sulphites are treated with acids, sulphur dioxide is produced :—



Sulphites are easily oxidized to sulphates by moist chlorine, nitric acid, chromic acid, and other oxidizing agents.

Formation of sulphuric acid. This acid was formerly made by the dry distillation of green vitriol (ferrous sulphate crystals, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The solid residue is ferric oxide, Fe_2O_3 . The resulting liquid is dilute sulphuric acid from which water is driven off on evaporation. Green vitriol received its name owing to its similarity to broken glass (Latin *vitrum*, glass) and the acid liquid obtained by distilling it was called *oil of vitriol*.



Crystals of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, are known as white vitriol, and those of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, as blue vitriol.

We have already seen that sulphuric acid can be produced by the oxidation of sulphurous acid. This may be done by (a) exposing it to air for a long time, (b) the action of mercuric oxide (p. 127), (c) nitric acid (p. 433), (d) moist chlorine (p. 433).

On the large scale nitric acid is used, but another method, involving the use of a catalyst, has recently been found to be commercially possible.

***Exp. 7.** To show the action of finely divided platinum on a mixture of sulphur dioxide and oxygen.

Required:—As in Fig. 95 and above; barium chloride, hydrochloric acid.

DIRECTIONS. Heat some platinized asbestos† in the tube B, and connect the bottle A with the oxygen and sulphur dioxide generators (or other supply of the gases), as shown in Fig. 95. The gases are dried by bubbling through conc. sulphuric acid contained in A, and the mixture passes over into B. The product is collected in the water in the flask c.

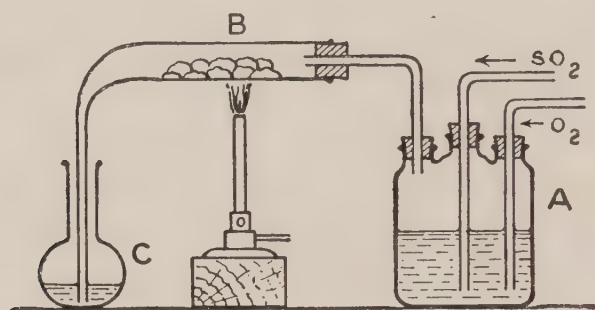


FIG. 95.

Note the thick white fumes produced. After 5 or 10 minutes test the liquid in c for sulphuric acid.

LABORATORY RECORD. Diagram of actual apparatus used; observations.

Questions:—(i) Is more than one substance likely to dissolve in the water in c?

(ii) How did you show that sulphuric acid has been formed?

(iii) Is your proof conclusive?

(iv) Write an equation for the action.

If the vapour be passed into a *dry* flask kept cool by a freezing mixture, it condenses into long white crystals. These combine with water with a hissing noise to form sulphuric acid.

* Demonstration.

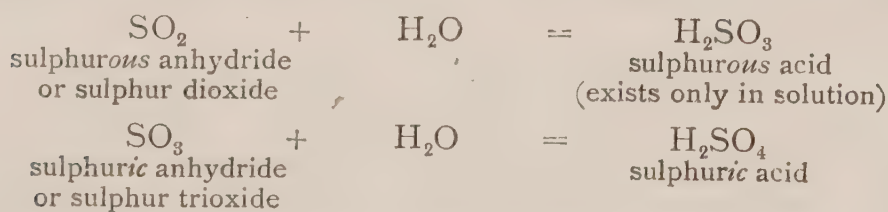
† See Appendix.

Catalysis. In Exp. 7 the metallic platinum remains unaltered, and apparently has taken no part in the chemical change, but the formation of sulphur trioxide would have occurred very slowly in its absence.

When a substance increases the rate at which a chemical change proceeds, without altering its own composition, it is called a *catalytic agent*, and the process is called *catalysis*.

Another example was observed in the preparation of oxygen (p. 107), when a mixture of potassium chlorate and manganese dioxide was heated. The oxide was found to be unchanged after the action, and thus acted as a catalytic agent. The real function of these agents is not fully understood.

Sulphur trioxide. The synthetical method by which sulphur trioxide was made in Exp. 7 shows that it contains a larger proportion of oxygen for a fixed amount of sulphur than does sulphur dioxide. Its molecular formula is SO_3 . On addition of water it yields sulphuric acid, showing it to be an acidic oxide like sulphur dioxide. It is consequently called *sulphuric anhydride*, just as the dioxide is termed *sulphurous anhydride*.



The salts of sulphurous acid are called *sulphites*;

„ „ sulphuric „ „ sulphates.

The former all contain the $-\text{SO}_3$ radical, and the latter the $-\text{SO}_4$ radical.

By the action of barium chloride on sulphuric acid (or soluble sulphates) the insoluble sulphate of barium is obtained, thus:—



Soluble sulphites, carbonates, and many other salts yield a white insoluble barium salt on addition of barium chloride. These, however, are nearly all soluble in hydrochloric acid, while barium sulphate is insoluble. A white precipitate formed by barium chloride in presence of hydrochloric acid is therefore used as **a distinguishing test for sulphates.**

Manufacture of sulphuric acid. The usual method employed for the manufacture of sulphuric acid is to oxidize sulphur dioxide with nitrogen peroxide in presence of steam.

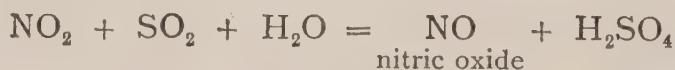
The raw materials needed are (1) iron pyrites, (2) air, (3) nitric acid (which yields nitrogen peroxide when acted on by sulphur dioxide), (4) steam.

Sulphur dioxide is produced by roasting iron pyrites (FeS_2) in excess of air:—



The hot mixture of air and sulphur dioxide is passed up a coke tower, down which a solution of nitrogen peroxide is trickling.

The oxide of nitrogen is carried on by the excess of sulphur dioxide and air into a large leaden chamber, where steam and more air are introduced. Here the main action occurs thus:—



The acid falls to the bottom of the chamber in a diluted state, while any unaltered gases pass on to a second chamber, where the action is completed. The residual gases are nitrogen and nitric oxide, and these are brought into contact with excess of air in a third chamber, where the nitric oxide is reconverted into the peroxide, thus:—



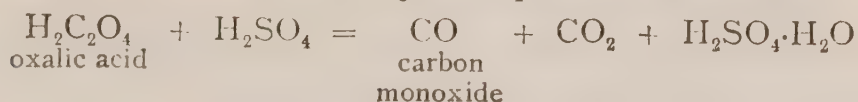
The gases then pass up a second tower, down which concentrated sulphuric acid is flowing. The latter absorbs the peroxide, and the solution is pumped up to the top of the first tower to be used over again.

It will be plain that the function of the nitric oxide is to act as a carrier of oxygen, by taking it from the air and giving it to the sulphur dioxide. The peroxide is used over and over again, and only needs occasional additions to make up for unavoidable wastage.

The dilute acid is heated first in glass and then in platinum retorts, in which the water distils off, leaving the commercial concentrated acid. It is liable to contain lead sulphate in solution, derived from the lead of the chambers. This salt is precipitated on diluting with water. It may also contain arsenic acid (H_3AsO_4), since arsenic is often present in iron pyrites. Arsenic oxide is formed along with sulphur dioxide, and forms arsenic acid on oxidation in presence of water. The commercial acid is often brown on account of bits of straw or other carbonaceous matter having accidentally been dropped into it.

The properties of sulphuric acid. At the ordinary temperature and pressure it is a colourless, oily liquid, having a specific gravity of 1.85. As usually manufactured it contains about 2 per cent. of water which cannot be removed by distillation; by cooling to 0°C . crystals of pure sulphuric acid separate.

It combines with *water* with great evolution of heat, forming a series of hydrates, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, &c. Its powerful affinity for water causes it to be a valuable desiccating agent, and it is used for drying air, oxygen, hydrogen, chlorine, hydrochloric acid, the oxides of carbon, and many other gases. This property also accounts for its charring many organic substances (e.g. paper, wood, sugar) containing carbon, hydrogen, and oxygen. It abstracts the two latter elements in the proportions in which they form water, leaving the black carbon behind. Its action on oxalic acid (p. 354) is similarly explained, and may be represented thus:—



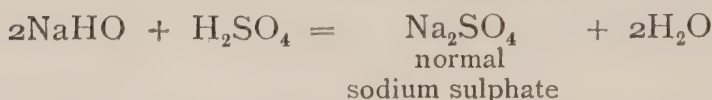
Its action with *metals* depends on the nature of the metal, the temperature, and the degree of dilution. Zinc, iron, and magnesium cause the liberation of hydrogen (p. 204) from the *cold diluted* acid, thus:—



A larger number of metals (e. g. silver, mercury, lead, tin) reduce the *hot concentrated* acid to sulphur dioxide in a similar manner to copper (p. 432). The *non-metals* carbon and sulphur, when heated with the concentrated acid, also cause the evolution of sulphur dioxide:—



With *basic oxides* and *bases* (i. e. metallic hydroxides) it reacts, like all acids, to form salts and water (p. 192). Thus:—



With *salts of acids which are volatile or easily decomposed*, such as carbonates, sulphites, chlorides, fluorides, and nitrates, sulphuric acid displaces, under varying conditions, the volatile acid and forms a sulphate. With carbonates (p. 336) it reacts, when cold and diluted, thus:—



With chlorides (p. 289), sulphuric acid, when concentrated and gently warmed, liberates hydrochloric acid:—



For its action on nitrates, see p. 390, sulphites, p. 436, fluorides, p. 310, bromides and iodides, p. 301.

The basicity of acids. It will have been noticed in dealing with various acids that some, such as sulphurous, sulphuric, and carbonic, form two kinds of salts with the same monovalent metal, e.g. sodium, whilst only one sodium salt of hydrochloric acid and one of nitric acid are known.

The molecules of hydrochloric and nitric acids contain only one atom of hydrogen capable of replacement by a metal, whilst there are two such hydrogen atoms in the molecules of carbonic, sulphuric, and sulphurous acids. Some acids possess hydrogen atoms in their molecules, which cannot be replaced by a metal to form a salt. Thus acetic acid ($\text{H}_4\text{C}_2\text{O}_2$) contains four hydrogen atoms per molecule, but only one can be replaced by sodium, when it is mixed with caustic soda. Hence it is necessary to distinguish between the total number of hydrogen atoms in a molecule of an acid, and the number of replaceable hydrogen atoms. The number of the latter, and therefore the number of salts the acid can form with the same monovalent metallic radical, is a measure of its **basicity**.

Thus hydrochloric and nitric acids can only form one series of salts, and are said to be *monobasic*; carbonic, sulphurous, and sulphuric acids form two series: (a) *normal* salts, in which the whole of the hydrogen is replaced by a metallic radical; and (b) *acid* salts or bi-salts, in which a part of the hydrogen of the acid still remains. These acids are said to be *dibasic*.

The basicity of an acid is ascertained by finding how many different salts it can form with the same monovalent metallic radical. With a divalent metal like zinc, copper, lead, &c., only one series of salts can be formed, even with a dibasic acid.

Hydrochloric acid forms NaCl				CuCl_2
Nitric	"	"	NaNO_3	$\text{Cu}(\text{NO}_3)_2$
Sulphuric	"	"	NaHSO_4 and Na_2SO_4	CuSO_4
Sulphurous	"	"	NaHSO_3 and Na_2SO_3	CuSO_3
Carbonic	"	"	NaHCO_3 and Na_2CO_3	CuCO_3

Exp. 8. To determine the basicity of hydrochloric and sulphuric acids.

Required :—Solutions of above acids and of potassium hydroxide of about equivalent strengths, methyl orange, burette, 25 c.c. pipette, microscope, slips of glass.

A. Using hydrochloric acid.

Put 25 c.c. of potassium hydroxide into each of two basins.

To one add two drops of methyl orange and exactly neutralize by adding hydrochloric acid from a burette.

Record the volume used and add twice this volume to the other basin.

Evaporate both nearly to dryness, and dissolve in a *very little* warm water. Put a drop of each liquid on a slip of glass, and watch the formation of crystals under the microscope. Observe whether they are all of the same shape or not.

Make drawings of the crystals in each drop.

B. Repeat, using sulphuric acid, but do a third experiment, adding three times the volume of acid used in the first. Make drawings of the crystals as seen under the microscope.

State the number of salts obtained in each case.

Carbon disulphide. This substance is made by passing sulphur vapour over red-hot charcoal. The vapour produced is condensed and purified from dissolved sulphur by distillation.

It is a colourless, mobile liquid, boiling at 46° C. It is very inflammable, burning in air with production of the dioxides of carbon and sulphur—



It is valuable as a solvent for sulphur, phosphorus, iodine, rubber, &c., which are insoluble in most other liquids.

QUESTIONS ON CHAPTER XXII.

[Assume that 1 gram-molecule of a gas occupies 22.4 l. at S.T.P.]

1. Give an account of the production of refined roll sulphur, starting with the sulphur-rock of Sicily.
2. Explain what is meant by 'allotropic form of an element'. Describe the preparation and properties of α , β , and γ sulphur.
3. How can the melting-point of sulphur be ascertained?
4. Describe the changes which occur when roll sulphur is heated from the ordinary temperature to its boiling-point (448°C.). Give an account of the 'phases' of sulphur.
5. Explain the meaning of 'synthesis'. Describe how hydrogen sulphide can be made synthetically, and give an account of its *physical* properties.
6. What volume of hydrogen at S.T.P. is required to combine with 100 g. of sulphur?
7. Describe fully the usual laboratory method for making sulphuretted hydrogen. State the conditions under which it reacts with (a) air, (b) copper chloride, (c) ferrous sulphate. Give equations.
8. What weight of hydrochloric acid is necessary to completely react with 100 g. of ferrous sulphide, and what volume of gas at S.T.P. would be obtained?
9. Mention three reactions of hydrogen sulphide which show it to be a reducing agent. Give a brief description of each, with equations.
10. Describe, in detail, how it can be proved that hydrogen sulphide contains its own volume of hydrogen, and show how the molecular formula for sulphuretted hydrogen has been established.
11. Describe the synthesis of sulphur dioxide, and give evidence for the conclusion that its molecular structure is correctly represented by the formula SO_2 .
12. Give a detailed account of the preparation of sulphur dioxide from sulphuric acid, and describe the *physical* properties of the gas. Draw a diagram of the apparatus you would use to prepare *liquid* sulphur dioxide.
13. What weight of copper is required to react with 150 g. of sulphuric acid, and what volume of gas at 15°C. and 740 mm. pressure would be obtained?
14. Describe and explain the action of sulphur dioxide on (a) sulphuretted hydrogen, (b) chlorine water, (c) vegetable colouring matters.
15. What volume of oxygen at 20°C. and 750 mm. pressure is required for the formation of 100 g. of sulphur dioxide?
16. Calculate the weight of sulphur in 20 l. of sulphur dioxide measured at 780 mm. pressure and 20°C.
17. Given solutions of sulphur dioxide and nitric acid, how could you make sulphuric acid?

18. What actions of moist sulphur dioxide show it to be a reducing agent? Explain the actions, if possible, by equations.

19. Compare the actions of sulphur dioxide and carbon dioxide on sodium hydroxide solution. Also compare the reactions of sulphites and carbonates.

20. How could you find whether a given solid was a sulphide, a sulphite, or a sulphate?

21. Calculate from the formulae the percentage composition of (a) sodium sulphite, (b) sodium bisulphite, (c) ferrous sulphide, (d) iron pyrites (FeS_2).

22. How could you distinguish between hydrochloric acid gas and sulphur dioxide; hydrogen and sulphuretted hydrogen; carbon dioxide and sulphur dioxide? Give as many methods as possible.

23. In what way could you purify sulphur dioxide from traces of sulphuretted hydrogen?

24. Compare the properties of iron pyrites and ferrous sulphide with regard to their action when (a) heated without air, (b) heated in air, (c) treated with hydrochloric acid.

25. Explain how solid sulphur trioxide can be obtained from dry sulphur dioxide and oxygen.

26. What is an 'anhydride'? Give four examples, with equations for their action on water.

27. Describe briefly the manufacture of sulphuric acid.

28. How can dry crystals of copper sulphate (blue vitriol) be obtained from copper, sulphuric acid, and water?

29. Give a general account of the physical and chemical properties of sulphuric acid.

30. What is meant by 'basicity of an acid'? Given solutions of sulphuric acid and caustic soda of known strength, explain fully how you would proceed to show that the acid is neither monobasic nor tribasic, but dibasic.

31. Calculate the volumes (at S.T.P.) of each gas remaining after the complete combustion of 1000 g. of carbon disulphide in the air of a room measuring 8 m. long, 6 m. wide, 3 m. high. Assume that air contains 21 per cent. of oxygen and 79 per cent. of nitrogen by volume.

CHAPTER XXIII

OZONE AND HYDROGEN PEROXIDE

Ozone. The oxygen set free during electrolysis of sodium hydroxide or sulphuric acid solutions has a peculiar smell, noticed also when electric discharges pass into the air from pointed conductors.

The smell is due to the presence of ozone (Gk. *ozein*, to smell), a gas which can contain nothing but oxygen, since it is formed when carefully purified dried oxygen is subjected to electric discharges.

Preparation. A convenient method of obtaining the gas is the apparatus invented by Brodie, of which a diagram is given (Fig. 96).

Carefully dried oxygen is passed into the apparatus at A and escapes at B. In passing through the narrow annular space it is subjected to a powerful electric strain, the dilute sulphuric acid in the vessel in C and D being severally in connexion with the poles of an induction coil.

Only a part of the oxygen is changed to ozone.

Properties. (a) The gas escaping at B has a strong seaweed-like smell, but on heating the tube B it becomes inodorous, showing that *heat destroys ozone*.

(b) When passed into a test-tube containing mercury, the clean surface of the metal is destroyed, and the metal clings to the glass. On heating the mercury, or on treatment with

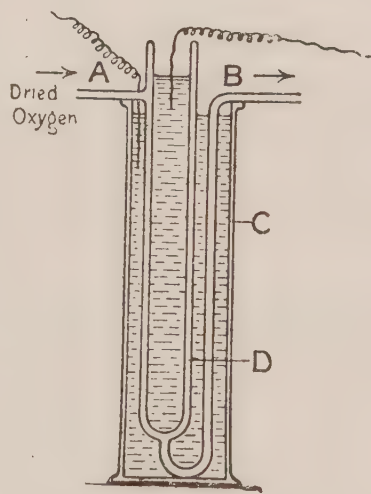


FIG. 96.

dilute sulphuric acid, it recovers its normal appearance. It can be shown that *mercury oxide* is formed.

(c) After sulphurous acid has been shaken with ozonized oxygen, the presence of sulphuric acid can be detected by addition of a solution of barium chloride acidified with hydrochloric acid.

(d) When passed into a weak solution of potassium iodide containing some phenol phthalein, the solution first becomes pink and later brown, proving formation of alkali (KOH) and iodine.

If this experiment is done so that the volume of gas before and after treatment with potassium iodide can be measured, it is found that there is no change in volume.

If ozonized oxygen is treated with turpentine oil a contraction in volume takes place and all the ozone is removed.

By making use of the latter fact and the action of heat on the gas the formula for ozone can be established, although there is always a large proportion of oxygen mixed with it.

Formula of ozone. 100 c.c. of a specimen of ozonized oxygen when treated with turpentine oil showed a contraction of 10 c.c. Thus 10 c.c. of ozone were present. When oxygen is ozonized a contraction takes place. Similarly, when ozonized oxygen is heated the original volume of oxygen is re-formed.

100 c.c. of the same specimen of ozonized oxygen gave 105 c.c. of oxygen when subjected to heat;

\therefore 10 c.c. of ozone give $105 - 90 = 15$ c.c. of oxygen.

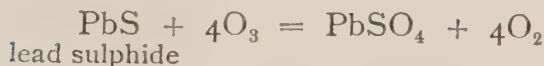
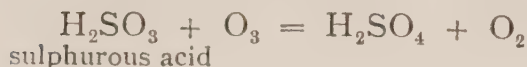
Let O_x be the formula for the ozone molecule;

$\therefore 10 O_x = 15 O_2 \quad \therefore 10x = 15 \times 2 \quad \therefore x = 3$

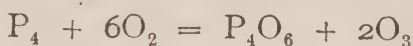
Hence, the molecular formula of ozone is O_3 .

Soret proved that the rate of diffusion of ozonized oxygen as compared with ordinary oxygen into chlorine corresponded to a density of 24 when oxygen has a density of 16. Hence the M.W. is 48, which gives a formula O_3 for ozone, confirming the previous result.

The reactions of ozone are shown by the equations below:—

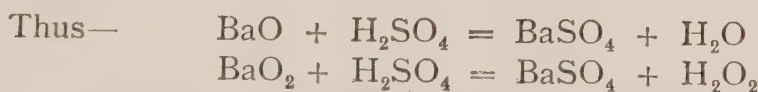


Ozone is formed by several other reactions. Thus when phosphorus glows in moist air, the following reaction takes place:—



In all its oxidations it is the one atom which is active, a molecule of oxygen being set free for each molecule of ozone which reacts.

Hydrogen peroxide. When basic oxides react with acids, hydrogen oxide and a salt of the acid are formed. Similarly, when certain peroxides, as those of barium and sodium, are treated with acids, hydrogen peroxide and a salt are produced:—



To prepare the solution of hydrogen peroxide, freshly precipitated barium peroxide is used.

Exp. I. Preparation of hydrogen peroxide.

Required:—Barium nitrate, sodium peroxide, ice, rapid filter, beakers, basin.

Half fill a beaker with distilled water, and put in several lumps of ice.

Add to the cold water in small quantities at a time 10 g. of sodium peroxide, stirring after each addition.

Now pour in excess of a fairly concentrated solution of barium nitrate until no more hydrated barium peroxide is precipitated.

Filter the liquid by rapid filtration and wash on the filter with several *small* quantities of cold water.

Turn out the solid cake into a basin, and add water to make a creamy liquid (*A*).

Now put 50 c.c. of sulphuric acid (1:4 of water) into a beaker, add several lumps of ice, and add *A* in *small* quantities with constant stirring until the *strongly acid reaction* is removed.

Filter through a Swedish filter-paper and put about 10 c.c. in a basin over sulphuric acid in a desiccator. Use the rest for Exp. 2.

Exp. 2. To examine the properties of a solution of hydrogen peroxide.

Required:—Solution of hydrogen peroxide, manganese dioxide, solutions of barium and calcium hydroxide, potassium chromate, sulphurous acid, potassium iodide, phenol phthalein; ether, carbon disulphide.

Put a few c.c. of the hydrogen peroxide into each of six test-tubes.

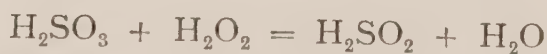
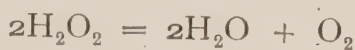
- A.* Examine the solution, **note** smell, reaction with litmus, and then boil and test issuing gas with glowing splinter.
- B.* Take the temperature, add manganese dioxide, and test the gas for oxygen. Again **record** the temperature of the liquid, and **observe** whether the manganese dioxide appears altered in any way.
- C.* Add barium hydroxide solution.
- D.* Add freshly made sulphurous acid. Test for sulphuric acid.
- E.* Acidify with dilute sulphuric acid and potassium iodide solution. Test for iodine by adding a drop of carbon disulphide and shaking.
- F.* Add an equal volume of ether followed by a few drops of potassium chromate, acidified with sulphuric acid. Shake gently, and describe the changes when the liquid has stood for 5 minutes.

- Questions:*—(i) What is the action of heat on hydrogen peroxide, supposing H_2O_2 is the formula? Give an equation.
- (ii) How do you account for the rise in temperature in *B*, supposing that the manganese dioxide remains unchanged?
- (iii) Give equations for *C*, *D*, and *E* (consider the action of ozone in the case of *D* and *E*).
- (iv) Which reaction would be a suitable test for hydrogen peroxide?

Properties of hydrogen peroxide. Hydrogen peroxide can be obtained free from water by evaporating over sulphuric acid *in vacuo*.

Thus prepared it is a viscous liquid, sp. g. = 1.46, exploding easily, especially when heated.

It oxidizes many substances readily and, like ozone, only one atom of oxygen in the molecule is used.



It decomposes with evolution of heat, i.e. it is an endothermic substance like ozone and acetylene.

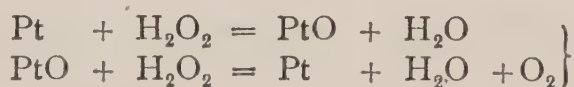
Catalytic decomposition of hydrogen peroxide. The influence of temperature on the rate at which a chemical change proceeds is very great, a rise of 10°C . approximately doubling the rate of change.

We may reasonably assume that a reaction which is influenced by temperature, and which does not sensibly proceed at the air temperature, really does so, but at too slow a rate for detection.

For example, a solution of hydrogen peroxide does not appear to decompose at the air temperature, but the addition of certain substances, such as platinum black, manganese dioxide, &c., so accelerates the change that the rate becomes measurable. Such accelerators are called catalysts or catalytic agents (see pp. 107, 439).

Several explanations have been given of the nature of such catalytic actions.

(1) *The intermediate compound theory.* The action of platinum, in the case of hydrogen peroxide, is supposed to take place thus:—



(2) *So-called contact action.* Brought about by the presence of fine powders. Thus a solution of gas under the influence of a fine powder gives up its gas. Such an action lies on the border between physical and chemical changes, and is not properly understood.

QUESTIONS ON CHAPTER XXIII.

1. Describe the preparation and properties of ozone.
2. State the evidence which leads to the conclusion that O_3 is the molecular formula of ozone.
3. How is hydrogen peroxide prepared? Compare its properties with those of hydrogen monoxide.
4. How would you distinguish between ozonized oxygen, and oxygen containing traces of the vapour of hydrogen peroxide?
5. Compare the reactions of ozone and hydrogen peroxide with (a) sulphurous acid, (b) potassium iodide, (c) lead sulphide.
6. Define catalysis and give a general account of the catalytic actions with which you are acquainted.

CHAPTER XXIV

THE METALS

Preliminary Questions.

1. Taking *sulphur* as a typical non-metal and *lead* as a typical metal, compare their properties on the following points:—

- (a) General appearance.
- (b) Density—whether high or low.
- (c) Melting-point—whether high or low.
- (d) Whether malleable or brittle.
- (e) Conductivity for heat and electricity.
- (f) Ability to combine with hydrogen.
- (g) Type of oxide produced—acidic or basic

2. How have you obtained—

- (a) Mercury, copper, lead, iron, from their oxides?
- (b) Copper, from a solution of its sulphate (a) without addition, (β) with addition of other substances?

3. Classify the methods (of question 2) for obtaining metals from their compounds.

4. What products would you expect to get by heating the sulphide of a metal (say lead sulphide) in a current of air or oxygen? How would you attempt to obtain the metal?

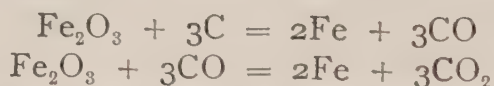
5. How would you attempt to get a metal from an ore which consists chiefly of its carbonate (say copper carbonate)?

Extraction of metals from their ores. Metals occur more frequently in their compounds with oxygen, sulphur, &c., than in the free state. These compounds, called ores, are often mixed with stony matter, from which they have to be separated either by hand-picking or some mechanical method which takes advantage of the difference in density, e.g. placing the crushed material in a stream of running water, which carries off the lighter stony matter, leaving the heavier ore behind.

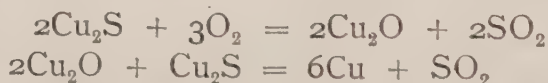
When thus separated the ore is *smelted*, i.e. subjected to chemical changes which result in obtaining the free metal. The particular course to be adopted depends on the composition of the ore and on the cost of the process.

Direct reduction. If the ore is an oxide or carbonate, it can often be reduced by heating with coke to a high temperature, adding, if necessary, some other substance or flux to assist in the melting, and to combine with any unseparated foreign matter. Thus iron ore, which is usually in the form of oxide or carbonate, is mixed with coke and limestone, and the whole heated in a blast-furnace in a current of air. The oxygen and coke give carbon monoxide, which reduces the oxide to metallic iron.

The limestone is converted to lime, and combines with the sand to form a silicate of calcium (called *slag*), which floats on the heavier metal.



Auto-reduction. When the ore consists of the sulphide, a portion of it is roasted (i.e. heated in a current of air) until it is partly converted into an oxide. This, on fusing with unaltered sulphide, results in formation of the metal and sulphur dioxide, e.g. :—



Electrolysis. This method is used for the manufacture of many metals which are difficult to reduce by carbon. The ore mixed with other suitable substances is melted in an electric furnace, and when liquid, electrolysis takes place. Sodium, potassium, calcium, aluminium, and magnesium are obtained in this way.

COMPOUNDS OF METALS.

Over 60 metals are known to exist, and of these about 24 may be described as common. Since each one can combine with a large number of other elements (both metals

and non-metals), and also with groups of others, as in salts, the total number of compounds is very great. Some compounds are easy to make and are stable (i. e. difficult to decompose) under the ordinary conditions of temperature, pressure, presence of air and moisture ; others are difficult to obtain, their formation being possible only under certain well-defined conditions.

Compounds of metals with metals. A molten metal is capable of dissolving other metals. In many cases definite compounds are formed which remain in solution. On cooling, the whole solidifies, forming an alloy. Most alloys may be regarded as a solidified solution of one metal in another, or of the compound of a metal in excess of the other.

Alloys. *Brass* is an alloy of copper and zinc.

Bronze contains copper, zinc, and tin.

Pewter contains lead and tin.

Gun-metal consists of copper and tin.

German silver contains copper, zinc, and nickel.

Amalgams. Mercury has the power of dissolving many metals ; the solutions are known as amalgams.

When the mercury is in excess they are liquid, but solids are formed if there is defect of mercury. Some are used for stoppings for teeth. Tin amalgam is used for making mirrors. An amalgam of sodium is often used as a reducing agent, for in the presence of water it produces hydrogen, but more slowly than pure sodium.

Compounds of metals with non-metals. These consist of oxides, hydroxides, and salts. In considering methods for their preparation it is necessary to know whether they are soluble or insoluble in water, so as to be able to fix on the most suitable course.

If they are insoluble or very slightly soluble, they are often made by double decomposition of some soluble salt of the metal and a soluble substance containing the non-metallic radical.

If they are soluble the substance is formed in solution and the water evaporated.

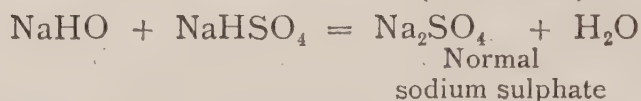
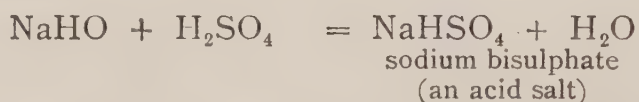
The following table of solubilities should be consulted when planning the preparation of a compound.

It is useful to remember that *all the common compounds of sodium, potassium, and ammonium are soluble; so also the nitrates of most metals.*

The oxides, hydroxides, and sulphides are insoluble, except those of sodium, potassium, and ammonium. Those of calcium, barium, and strontium are slightly soluble.

Classification of salts. A salt has already (p. 182) been defined as a solid derived from an acid by replacing the hydrogen of the acid by a metal. This primary idea of a salt needs qualification and extension in view of subsequent knowledge.

When the acid contains more than one replaceable hydrogen atom per molecule, i. e. when the acid is di-, tri-, or tetra-basic, salts are obtainable in which only a portion of the total replaceable hydrogen in a molecule is replaced. Such salts are called **acid salts**, while those in which all the replaceable hydrogen has been replaced are known as **normal salts**. Thus from sulphuric acid and sodium hydroxide two salts can be formed—



NaHCO_3 (p. 346), Na_2HPO_4 (p. 414), $\text{NH}_4\cdot\text{HSO}_4$ are examples of acid salts. These salts do not necessarily show an acid reaction with litmus, the word 'acid' being used to indicate the presence of acidic hydrogen.

Since ammonium plays the part of a metal, definitions must be made to include ammonium salts by making 'positive radical' alternative with metal. Hence we may say that:—

An acid salt is a compound derived from an acid by the substitution of a metal or other positive radical for **a portion** of the replaceable hydrogen in a molecule of the acid.

A normal salt is a compound derived from an acid by the substitution of a metal or other positive radical for **all** the replaceable hydrogen contained in a molecule of the acid.

In addition to these types of salts are found a large number which contain a larger proportion of metal than the normal salt contains. These are more especially formed when the metallic base is weak. They are called **basic salts** and may be considered as compounds of the normal salt with the metallic oxide or hydroxide. For example, the precipitate obtained by the action of sodium carbonate solution on a solution of a copper salt (p. 339) is not the normal salt CuCO_3 , but $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; the normal salt is not known to exist.

In many cases basic salts are formed from a normal salt by the action of water, with simultaneous formation of free acid. Such actions are examples of **hydrolysis** (see pp. 486, 489, 492, &c.).

A basic salt is one in which the proportion of the positive radical to negative radical is greater than in the corresponding normal salt.

Double salts are derived from other than monobasic acids by replacing the hydrogen by more than one positive radical, e.g. KNaSO_4 , $\text{Mg}(\text{NH}_4)\text{PO}_4$ are double salts. Some double salts (e.g. the alums, *q.v.*) may be regarded as molecular compounds; thus common alum, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, is a compound of aluminium sulphate, potassium sulphate, and water.

SOLUBILITY (APPROX.) OF SOME METALLIC SALTS AND HYDROXIDES IN GRAMS
PER 100 GRAMS OF WATER AT 15° C.

	Li	Na	NH ₄	K	Ag	Ca	Sr	Ba	Mg	Zn	Pb
Cl	75.25	35.7	35.2	32.4	10 ⁻⁴	70	50	34.6	54	350	0.9
Br	169	87	70	62.5	8 × 10 ⁻⁶	137	96	102.5	95	426	0.73
I	161	174	—	140	2 × 10 ⁻⁷	201	172	194	110	470	0.06
F	0.26	4.3	—	92	181	0.001	0.01	0.16	0.007	1.6	0.06
NO ₃	66	83	161.5	26	195	117	61	8	72	111	51
OH	12.7	63.5	—	107	0.002	0.17	1.5	3.23	8 × 10 ⁻⁴	4 × 10 ⁻⁴	—
SO ₄	34	13.4	74.2	10.1	0.7	0.2	0.01	2 × 10 ⁻⁴	33.8	50.8	0.004
CO ₃	1.4	13.4	100	110.5	0.003	0.001	9 × 10 ⁻⁴	0.002	0	0.001	10 ⁻⁴

General methods of preparing salts, &c. It is useful to know the following general methods. They are not applicable in all cases; the exceptions will be noticed under the individual metals.

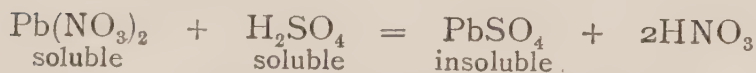
Chlorides, nitrates, and sulphates.

I. If soluble in water :—

- (a) By the action of the acid on the *metal*. In some cases the action is too slow to be useful.
- (b) By the action of the diluted acid on the *oxide*, *hydroxide*, or *carbonate*. This is nearly always possible.

II. If insoluble in water :—

- (c) By double decomposition of some other salt of the metal which is soluble, and a soluble chloride or sulphate, e. g. :—

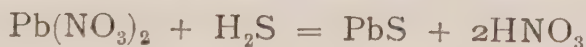


Sulphides. (a) Those of Na, K, Ca, Sr, Ba, Mg, Al are soluble in or decomposed by water, and are prepared by special methods.

(b) Those of iron, nickel, cobalt, zinc are soluble in acids, and can only be prepared in presence of an alkali, such as ammonium hydroxide. To a solution of some soluble salt add ammonium hydroxide till alkaline, and then ammonium sulphide. A precipitate of the sulphide is formed, e. g. :—



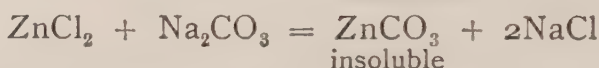
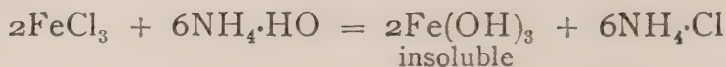
(c) The rest are made by passing hydrogen sulphide into a dilute solution of any soluble salt of the metal, e. g. :—



Hydroxides and carbonates. (a) Those of the alkali metals, being soluble, are manufactured by special methods (Ch. xxv).

(b) The rest are nearly all insoluble, and are made by

double decomposition with the corresponding alkali compound, e.g. :—



Oxides. (1) By heating the nitrate, e.g. :—



Exceptions: the nitrates of the alkali metals and ammonium.



When the oxide is itself decomposed on heating, e.g. HgO , careful regulation of the temperature is required.

(2) By heating the carbonate :—



Exceptions: the normal carbonates of the alkali metals, Na_2CO_3 , K_2CO_3 , which are unchanged by heat.

(3) By heating the hydroxide, e.g. :—



Exceptions: sodium and potassium hydroxides.

(4) Direct oxidation of the metal is not often employed in the laboratory, since the action is liable to be superficial only. It may be used for cupric oxide, and also for litharge (PbO) on the large scale.

Practical hints for the preparation of salts, &c.

(1) *A clear idea of the method* you are going to adopt is the first essential. In cases of doubt try preliminary experiments with *small* quantities to test the practicability of your scheme.

(2) *Quantities.* If a definite amount has to be prepared, roughly weigh one of the original materials, and allow a little over for possible loss. Much time is often wasted by not paying attention to this point.

It is often necessary to consider which of two materials should be in excess; e.g. in making zinc sulphate crystals

from zinc and sulphuric acid the zinc should be in excess. When the action is over, the excess of metal can be removed by filtration before crystallizing. If the acid had been in excess the crystals could not easily be separated from the non-volatile sulphuric acid. As a rule, when dealing with a solid and a liquid, it is best to have excess of the solid and to separate by filtration.

(3) *Neutrality of salts to litmus.* The normal sodium, potassium, and ammonium salts of the powerful acids (e.g. sulphuric, nitric, hydrochloric, oxalic) are soluble in water and neutral to litmus. The neutral point can be ascertained by removing a drop of the solution on a glass rod to a litmus-paper.

Very few other salts are quite neutral, and the litmus test is useless. In these cases one of the materials is usually a solid, and the cessation of effervescence, or other visible action (the solid being in excess), is taken as evidence of the completion of the action.

In the case of carbonates the solution should be heated to drive off any carbon dioxide which has dissolved in the water, and the point of neutrality finally tested afterwards.

(4) *Crystallization.* The best conditions for obtaining good crystals from a solution are :—

(a) Slow evaporation, such as is obtained by leaving a solution just saturated at the air temperature to stand in dry air.

(b) Avoidance of agitation.

(c) The removal of all but one of the crystals which first form.

In preparing crystals in a limited time, it is usual to evaporate quickly until a drop of the liquid crystallizes at once when removed on a glass rod. It is often better to carry the evaporation a little too far rather than the reverse, since it is always possible to add a little more of the solvent, reheat, and then cool. Some solids do not crystallize easily without agitation or unless the vessel is scratched with a glass

rod. When the crystallizing point has been found, larger crystals are obtained by allowing the solution to cool slowly than by cooling rapidly.

Sometimes, especially when heat is to be avoided or when a substance crystallizes with difficulty, alcohol will cause crystallization. Very few salts are soluble in alcohol, and most are rendered less soluble in water if alcohol is present.

(5) *Precipitation, decantation, and filtration.* When a substance is prepared by precipitation it has to be separated from the solvent and any other solid which remains in solution. The precipitate may be powdery (often as minute crystals), curdy, flocculent (i. e. fleecy), or gelatinous. In order to separate the solid from the solvent quickly, it is usually best to precipitate from a hot well-stirred solution. The particles cohere and subside quicker when this is done.

In adding the precipitating agent (precipitant), care should be taken to avoid excess, otherwise the washing process may be long and tiresome. If the precipitate has subsided well, washing by decantation is the quicker method, but it should be transferred finally to a filter and the washing completed there.

If the precipitate does not subside, the washing must be done entirely on a filter. In such cases rapid filtration apparatus should be used.

CHAPTER XXV

SODIUM AND THE ALKALI METALS

Preliminary Questions.

1. What is the chief natural sodium compound, and where does it occur?
2. Describe the properties of sodium as far as you have already observed them.
3. Would you expect free metallic sodium to exist in Nature or not? Give reasons for your answer.
4. How are sodium and potassium detected in their compounds?
5. What are the characteristics of an alkali?
6. How can the carbonate and bicarbonate of sodium be made from caustic soda, and what are their uses?
7. How can normal sodium sulphate and sodium bisulphate be made?

The alkali metals. Sodium and potassium are the best-known metals in this group. The others, viz. lithium, caesium, and rubidium, only occur in small quantities, though they are widely distributed. The resemblances both between the elements and between their compounds are more noticeable than the differences. A knowledge of the properties of sodium and its compounds gives a good idea of the general properties of the group.

Sources. Sodium occurs in common salt, NaCl , found in sea-water; and as rock salt in Cheshire, Siberia, &c. 1000 parts of sea-water yield about 36 parts of solid matter on evaporation, of which about 26 parts consist of sodium chloride. Potassium chloride, KCl , is found as a solid, called sylvine, in Germany.

The nitrates NaNO_3 and KNO_3 are found in Chili and India respectively. The latter is known as nitre or saltpetre, and the former as caliche or Chili saltpetre.

Potassium compounds are found in the ashes of trees and most land plants; sodium salts in the ashes of marine plants.

Lithium, rubidium, and caesium occur in certain mineral waters, in the ash of tobacco and other plants.

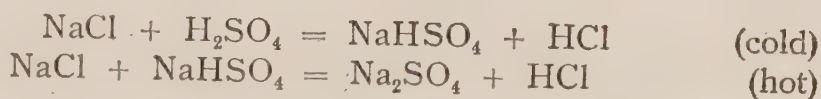
Sodium chloride. In the crude condition it is obtained by allowing sea-water to evaporate in shallow pits which are filled at high tide. The crystals are removed by a sort of shrimping-net when the sun has caused sufficient evaporation.

To obtain the substance from rock salt the mines are (in some cases) filled with water, which dissolves the sodium chloride, leaving the insoluble clay, &c. This solution (brine) is pumped up and evaporated in the sun and wind by allowing it to trickle over piles of brushwood. The process is completed by the application of artificial heat.

In neither case is the product pure sodium chloride. To purify it a saturated solution is made, and twice its volume of hydrochloric acid solution added. Crystals of sodium chloride are precipitated, while the other solids (magnesium chloride and sodium sulphate) remain in solution.

Properties. Sodium chloride and the other chlorides of this group are white solids which crystallize in cubes. They melt easily, but are not decomposed by heat; on electrolysis they yield the metal and chlorine.

By the action of concentrated sulphuric acid, the normal or acid sulphates are formed with liberation of hydrogen chloride. Thus,



Common salt is the chief commercial source of chlorine, from which bleaching powder and other chlorine compounds are made. It is also the starting-point in the manufacture of many important sodium compounds, e.g. the carbonates, hydroxides, sulphates, &c.

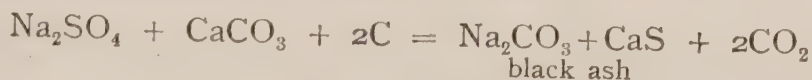
Sodium carbonate, *washing soda*, or *soda crystals*. This substance appears to have been known from very ancient times; a natural form occurring in Egypt was used to make glass. In Europe it was formerly obtained from the ashes of sea-weed. It is manufactured to-day in enormous quantities in South Lancashire and Cheshire, by three distinct processes, common salt being the source of sodium in each of them.

Leblanc process. (a) Salt is heated with sulphuric acid.



The acid is a valuable by-product, and is used to make chlorine compounds.

(b) The salt-cake is mixed with powdered coal and limestone, and heated in a revolving furnace.



(c) Water is added to the black ash, in which the carbonate alone dissolves. The solution is evaporated to obtain soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

Solvay or ammonia-soda process. (a) Ammonia gas is passed up a tower down which brine is trickling. Carbon dioxide

is bubbled into the double solution of brine and ammonia under pressure, when the following reaction occurs:—



The bicarbonate being less soluble than the ammonium chloride crystallizes out first.

(b) The bicarbonate is heated to get the normal salt.



The carbon dioxide is used over again for (a), together with some obtained from limestone.



The lime produced is used to liberate the ammonia from the chloride produced in (a).

Thus the process is very economical, but there is no valuable by-product like the hydrochloric acid in the Leblanc process.

Hargreave's process. The pure caustic soda produced electrolytically (p. 467) is allowed to absorb carbon dioxide.



Properties and uses. Normal sodium carbonate forms large monoclinic crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, which effloresce (i.e. lose water) in dry air. Its solution in water is alkaline to litmus. With acids it forms sodium salts, carbon dioxide being liberated.

It is used in the manufacture of soap and glass, and for softening 'permanently' hard water—hence its name 'washing soda'.

Sodium bicarbonate, or baking soda, NaHCO_3 . It is manufactured (a) by the Solvay process as above, or (b) by passing carbon dioxide over soda crystals in the cold.



Properties. A white crystalline anhydrous solid, much less soluble in water than the normal salt. On heating the solid,

or the solution, it readily gives off carbon dioxide and water to form the normal salt.



It is used for making baking powder and in medicine.

Sodium hydroxide or caustic soda. This substance is now manufactured on the large scale by the Castner process, which consists in the electrolysis of a saturated solution of common salt. The cell is divided into three compartments. The two outer ones each contain a carbon anode surrounded by brine; chlorine is produced on the anode and led off for the manufacture of bleaching powder, &c., while the sodium combines with mercury, which lies at the bottom of the whole cell. The central compartment contains an iron kathode surrounded by pure water. By rocking the cell the mercury amalgam flows under the partitions into the water, and is attracted by the kathode. Here the sodium reacts with the water, yielding caustic soda and hydrogen.



The solution is evaporated, and the melted hydroxide cast into sticks. The product only contains 0.5 per cent. of impurity.

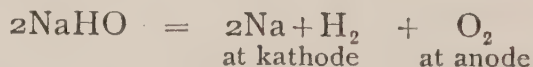
Potassium hydroxide, or caustic potash, KHO, is made in a similar manner, starting with potassium chloride, KCl.

Properties. Sodium hydroxide and the hydroxides of the other metals of this group constitute the alkalis. They exhibit a gradation of properties, but the differences are slight. They are white, deliquescent solids, possessing a 'soapy' touch, and melt without decomposition. They dissolve readily in water, the solution turning red litmus blue and yellow turmeric paper brown. On exposure to air they rapidly absorb carbon dioxide, forming a carbonate, and they react with all acids forming a salt and water. On heating a solution with oils or fats, saponification occurs (p. 350), i.e. a soap is formed, the soap being an alkali salt of an organic acid; glycerin or similar bodies are simultaneously formed. Their solutions

precipitate the insoluble metallic hydroxides when mixed with solutions of other metallic salts, and on warming with ammonium salts ammonia gas is liberated.

Caustic soda is used largely in soap-making, and caustic potash in the manufacture of soft soap. The term 'caustic' results from the fact that they dissolve skin and flesh; they are used in surgery for removing blemishes from the skin.

Metallic sodium. Formerly the metal was manufactured by heating sodium carbonate with carbide of iron to a very high temperature. This has now been replaced by a modification of the electrolytic method by which Sir Humphry Davy first discovered the metal in 1807, viz. by the electrolysis of fused caustic soda.



The plant for the new process was invented by Castner.

For *properties* of the alkali metals see p. 470.

Oxides of sodium. When the metal burns in oxygen or a rapid current of air, the yellowish-white peroxide, Na_2O_2 , is formed. With water, caustic soda and oxygen are formed,



unless the water is kept very cold (see p. 450), when it dissolves unchanged. It is largely used as an oxidizing and bleaching agent in presence of water.

The monoxide, Na_2O , is obtained by heating the nitrate, NaNO_3 , with sodium in absence of air, nitrogen being evolved. It combines with water, forming caustic soda. The oxides of potassium, K_2O_4 and K_2O , are prepared in a similar manner.

Sodium sulphates. The normal salt is prepared by neutralizing dilute sulphuric acid with the hydroxide or carbonate. It crystallizes from water as the deca-hydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, known as Glauber's salt.

On adding an exact equivalent of sulphuric acid to one equivalent of this salt (see p. 444), the bisulphate is formed.

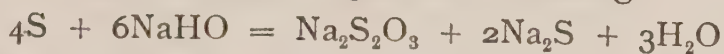


The bisulphate is strongly acidic to litmus, while the normal salt is neutral.

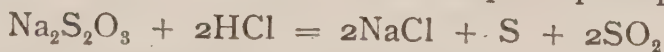
On reducing the normal salt with carbon, solid sodium sulphide, Na_2S , is formed.

The analogous potassium compounds, K_2SO_4 , KHSO_4 , K_2S , are made in a similar manner.

Sodium thiosulphate (or hyposulphite), $\text{Na}_2\text{S}_2\text{O}_3$, is prepared by boiling sulphur with caustic soda solution; crystals of 'hypo' ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) separate on cooling.



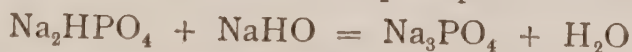
A solution of this salt is used for fixing photographic plates after development. Any unaltered silver chloride or bromide is dissolved by the hypo solution, leaving the parts which have been affected by light on the plate. With dilute acids sulphur dioxide is evolved and sulphur precipitated.



It is used in bleaching as an 'antichlor' (see p. 435).

Sodium pyro-borate or borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, occurs in the native state, and can be obtained by the action of boric acid on sodium carbonate. It is used as a glaze for porcelain, in soldering, in certain tests for metals known as borax bead tests, and as an antiseptic.

Sodium phosphates. The chief phosphate of soda is disodium orthophosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, formed by the action of phosphoric acid on sodium carbonate. On evaporating one equivalent of it with an equivalent of sodium hydroxide, crystals of the normal phosphate are obtained.



Similarly, on evaporating with an equivalent of the acid, the mono-sodium salt is obtained.



Ammonium compounds. The salts formed by the action of ammonia gas on acids bear distinct resemblances to the corresponding salts of the alkali metals. The chief obvious difference is in the volatility of ammonium salts when heated.

The halogen compounds, $\text{NH}_4\cdot\text{Cl}$, $\text{NH}_4\cdot\text{Br}$, $\text{NH}_4\cdot\text{I}$, crystallize in cubes like the haloid salts of sodium and potassium, i.e. they are *isomorphous* with them.

A solution of ammonia in water precipitates insoluble metallic hydroxides, just like solutions of sodium and potassium hydroxides. For this reason ammonia solution is supposed to contain ammonium hydroxide, $\text{NH}_4\cdot\text{HO}$. Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, and the bicarbonate, $\text{NH}_4\cdot\text{HCO}_3$, are formed by passing carbon dioxide into ammonia solution.

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is largely used as a fertilizer (see p. 373). The sulphide, $(\text{NH}_4)_2\text{S}$, is formed by passing hydrogen sulphide into ammonia solution. It has the power of dissolving sulphur, giving yellow polysulphides similar to those of potassium.

If mercury be used as the kathode in the electrolysis of an ammonium salt, the so-called 'ammonium amalgam' is formed. It has not been found possible, however, to isolate the ammonium radical, NH_4 , from this; a mixture of ammonia and hydrogen results.

Properties of the alkali metals. The five metals are very similar in their more obvious physical properties. They are light, white, lustrous, and soft at ordinary temperatures. They are readily melted, and are volatile at high temperatures, yielding characteristic flame colorations. Their electropositive character increases with increase of atomic weight; thus lithium and sodium tarnish rapidly in air, but rubidium and caesium spontaneously inflame. They all decompose cold water with evolution of hydrogen; the heat of reaction is not enough to ignite the gas in the cases of lithium and sodium, but does so in the cases of potassium, &c. Their affinity for chlorine also increases with the atomic weight.

Their salts are all soluble in water, and those derived from the same acid are usually isomorphous. The metals all unite with mercury, forming amalgams.

The dissimilarities are few; certain compounds of lithium and sodium (e.g. alums, platino-chlorides, &c.) are more soluble than those of potassium, rubidium, and caesium. Lithium compounds are related in physical properties to those of calcium and magnesium. Sodium combines less readily with the halogens than potassium, and sodium hydroxide does not always react like potassium hydroxide.

Practical problems. 1. From the sea-salt provided make a specimen of pure sodium chloride.

2. Make a specimen of solid caustic soda by the action of milk of lime (calcium hydroxide mixed with water) and soda crystals. Test the product to find whether it is free from calcium and from carbonate.

3. Prepare a specimen of solid sodium bisulphate, starting with sodium carbonate and sulphuric acid. Investigate the nature of the products formed by strongly heating the specimen.

4. Starting with sulphur and caustic soda solution, prepare crystals of sodium thiosulphate. Investigate the action of a solution on silver chloride.

5. Investigate the colours formed by *traces* of oxides of copper, nickel, cobalt, iron, and manganese on a bead of borax made by heating the salt on a loop of platinum wire. Having obtained a transparent bead, add a trace of the oxide to be examined, and heat it first in the oxidizing blow-pipe flame, and then in the reducing flame. Note the colours in each case. These are used as tests for the presence of the above metals.

6. Examine the flame colorations of as many of the alkali metals as possible, preferably with a spectroscope.

QUESTIONS ON CHAPTER XXV.

1. Explain how soda crystals can be manufactured, starting with common salt.
2. Describe the method of manufacturing sodium bicarbonate by Solvay's process. Compare the properties of this substance with those of the normal carbonate.
3. Describe as many methods as possible by which sodium chloride could be obtained in the laboratory. Give equations.
4. How is metallic sodium prepared? Give an account of its physical properties, and its action on water, air, oxygen, chlorine, and mercury.
5. Give an account of the manufacture of caustic soda; describe its properties, and state its action with carbon dioxide, chlorine, acids, and solutions of metallic salts.
6. Write a general account of the properties of the alkali metals and their compounds from the point of view of the periodic law.
7. Point out the resemblances of the ammonium compounds to those of the alkali metals.

CHAPTER XXVI

CALCIUM AND METALS OF THE ALKALINE EARTHS

Preliminary Questions.

1. Name the calcium compounds which occur in (*a*) limestone, (*b*) bone, (*c*) calcite, (*d*) hard water, (*e*) fluor-spar, (*f*) selenite.
2. How is calcium oxide manufactured? What is its action on water? What are its uses in chemistry?
3. Starting with the oxide, indicate how you would prepare the (*a*) chloride, (*b*) carbonate, (*c*) sulphate, of calcium.
4. Describe the action of carbon dioxide on a solution of calcium hydroxide.
5. What calcium compound is used in the preparation of acetylene?

Metals of the alkaline earths. *Alkaline earth* is a term formerly given to certain substances, including lime, strontia, and baryta—the oxides of calcium, strontium, and barium—then thought to be elements. These earths or oxides combine with water, forming hydroxides which are slightly soluble and which have an alkaline reaction with litmus. The metals were first isolated in 1808 by Sir Humphry Davy by the electrolysis of their fused chlorides. It is only recently that improvements in this method have resulted in the production of calcium in considerable quantity from fused calcium chloride.

Calcium, which may be regarded as typical of the group, is a brass-yellow, hard, malleable solid. It acts rapidly on water, with formation of hydrogen and the hydroxide. It tarnishes in moist air, and combines energetically when heated with hydrogen, oxygen, nitrogen, and chlorine. When burnt in air it combines with both oxygen and nitrogen, as magnesium does. The nitride yields ammonia on addition of water.



Sources. Calcium occurs abundantly in its carbonate as limestone, marble, chalk, &c.; in gypsum or selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; in fluor-spar, CaF_2 ; in silicates, &c.

Strontium is found in strontianite, SrCO_3 , at Strontian in Scotland. Barium occurs principally in heavy-spar, BaSO_4 , often associated with galena, PbS , a common ore of lead.

Calcium carbonate. This is the most convenient substance from which to prepare the other compounds of calcium. It occurs in two crystalline forms, viz. (a) rhombohedrons, with three cleavage planes, as in calcite and Iceland spar; (b) rhombic prisms, as in arragonite. It is therefore *dimorphous*. *Limestone* is calcium carbonate mixed with varying quantities of sand, clay, &c. *Chalk* consists of the skeletons of minute sea animals which absorbed calcium carbonate from the water. *Marble* is a crystalline variety of limestone probably formed by the action of heat and pressure. Coral,

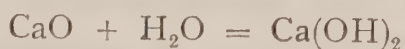
egg-shells, oyster-shells, &c., are largely composed of calcium carbonate.

Preparation of pure calcium carbonate from limestone. The limestone is dissolved in hydrochloric acid, the insoluble sand and clay being removed by filtration. Ammonia solution is added till the mixture is alkaline, and any precipitated hydroxides of iron or aluminium filtered off. Ammonium chloride solution is then added to prevent the precipitation of magnesium, and then on adding ammonium carbonate solution a precipitate of pure calcium carbonate is obtained. This is washed and dried.

Properties. Prepared as above the precipitate is at first amorphous, but, on standing, crystals resembling calcite form if the solutions were cold; if warm the less stable arragonite form is produced. It is practically insoluble in cold water, but water containing carbonic acid dissolves it, and the bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, is supposed to be in solution. When heated to high temperature in a closed vessel it dissociates into oxides of calcium and carbon (see p. 387). It is used largely in the manufacture of lime, and as a flux in smelting metallic ores.

Calcium oxides and hydroxide. The monoxide, or quicklime, CaO , is prepared on the large scale as described on p. 334. If the original carbonate is pure (as are certain kinds of marble and calcite), the pure oxide is obtained. It is very difficult to fuse and to reduce, but has been vaporized in the electric furnace. On heating it glows brightly, giving the intense and well-known limelight. It is a very bad conductor of heat.

On addition of water the hydroxide (slaked lime) is formed with considerable liberation of heat (see p. 169).



This is slightly soluble in water, forming lime-water. A mixture of water and excess of slaked lime is known as *milk of lime*. It is used for making mortar and cement.

Mortar is a mixture of slaked lime, sand, and water. On exposure to air it becomes hard, owing to formation of the carbonate.



Water is liberated until the change is complete. The sand makes the mortar porous, and provides access for the gas to the interior. The carbonate crystals adhere to the sand, and a compact hard mass results. The sand also prevents cracking from shrinkage on formation of the carbonate. A small amount of calcium silicate also forms.

Cement is made by heating together limestone, sand, and clay, and then powdering the mixture. On addition of water it sets hard without the assistance of any gas. Hence it can be used for masonry below water-level. When set it consists of silicates of calcium and aluminium.

Calcium dioxide, CaO_2 , can be obtained by the action of hydrogen peroxide on lime-water.

Calcium chloride, CaCl_2 , is obtained as a by-product in several manufacturing processes, notably in the ammonia-soda process. In the laboratory it is made by the action of marble or lime on hydrochloric acid. On evaporating to dryness a non-crystalline porous mass is obtained. It is largely used for drying gases, &c., owing to its power of combining with water to form a series of hydrates, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, which form crystals. It also combines with ammonia, forming $\text{CaCl}_2 \cdot 8\text{NH}_3$, so that it cannot be used to dry this gas. With sulphuretted hydrogen it forms calcium sulphide and hydrogen chloride, hence phosphorus pentoxide is used to dry hydrogen sulphide.

Bleaching powder (chloride of lime), Ca(OCl)Cl . This is an important commercial substance, since it enables chlorine to be distributed to bleaching works as part of a solid instead of the much more bulky gas. It is manufactured by passing slaked lime thinly laid on mechanical 'conveyors' through chambers, in the opposite direction to which a stream of chlorine is flowing.

The gas is liberated on addition of a diluted acid. In bleaching, the material is passed through troughs containing a dilute solution of bleaching powder and then through troughs containing weak hydrochloric or sulphuric acids.

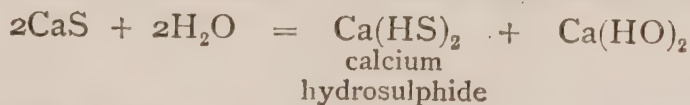


Dry bleaching powder has the composition expressed by the above formula. It is not a mixture of the chloride and hypochlorite, though it splits up into these on addition of water.

Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is a very soluble and deliquescent solid formed by the action of nitric acid on the carbonate.

Calcium sulphate, CaSO_4 , occurs in the anhydrous state as anhydrite, and crystallized with water as selenite or gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; satin-spar and alabaster are crystalline varieties of the hydrated salt. It can be obtained artificially by precipitation, since it is only slightly soluble in water. On heating gypsum to 125° , until nearly all the water of crystallization has been driven off, a powder known as *plaster of Paris* is obtained. When this is mixed with water recombination occurs, a hard rigid solid being formed. This is largely used for making casts of statuary, &c., and in surgery. If the temperature during formation is too high, and if *all* the water is driven off, recombination does not occur, and the plaster is said to have been 'dead-burnt'.

Calcium sulphides. The monosulphide, CaS , is formed by reducing calcium sulphate with charcoal, or by passing hydrogen sulphide over heated lime. It is a white solid, sparingly soluble in water. It reacts with water thus:—



On heating it shines in the dark, especially in presence of traces of other salts, such as borax; for this reason it used to be known as *Canton's phosphorus*.

By boiling milk of lime with sulphur, the disulphide, CaS_2 , and the pentasulphide, CaS_5 , may be obtained.

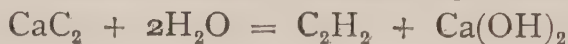
Calcium phosphates. Tricalcium orthophosphate, $\text{Ca}_3(\text{PO}_4)_2$, is the most important of the many phosphates of calcium. It occurs as the mineral phosphorite and apatite, a double salt with calcium fluoride, $3\text{Ca}_2(\text{PO}_4)_2 \cdot \text{CaF}_2$, and is a constituent of many rocks. By the decomposition of these rocks it gets into the soil, and although insoluble in pure water it dissolves in water containing common salt and carbonic acid. Thus it is absorbed by the roots of plants, and thence into the bodies of animals, where it goes to build up the bones. Bone-ash contains about 83 per cent. of this salt.

It may be prepared by precipitation from solutions of sodium phosphate and a soluble calcium salt. When bone-ash is treated with unconcentrated sulphuric acid, a mixture of calcium sulphate and monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, is obtained. This is known as *superphosphate of lime*, and is largely used as a fertilizer. The monosalt is more soluble than the tricalcium salt.

Calcium carbide, CaC_2 , is now manufactured on the large scale by the interaction of finely powdered limestone or lime with coke in an electric furnace.



It is chiefly used for making acetylene by the action of water.



When heated in nitrogen calcium cyanamide, CaC_2N_2 , is formed; it is used as a fertilizer.

Strontium and barium compounds. The oxides, hydroxides, carbonates, chlorides, nitrates, and sulphates are obtained by methods similar to that for the corresponding calcium salt. Their properties are very similar, slight differences in solubility, their spectra, and molecular weights being the only means of distinction.

The atomic weight of strontium is 87.6, being nearly the mean of those of calcium (40) and barium (137.4). The electro-positive character increases with the atomic weight. They all decompose water with liberation of hydrogen, and burn in air.

Reference to the table of solubilities (p. 458) will show that the solubility of the hydroxides increases with increase of the atomic weight of the metal, while for most of the other compounds the reverse is true.

Practical problems. 1. Examine the flame colorations of calcium, strontium, and barium, using their chlorides. Find the effect of looking at the calcium and strontium flames through blue glass.

2. Prepare a specimen of plaster of Paris from powdered gypsum, by heating to 125°C . Heat another lot strongly for some time. Compare their action on water.

3. From the limestone provided prepare a sample of pure calcium carbonate.

4. Starting with calcium carbonate, make 5 grams of (a) calcium phosphate, (b) calcium sulphate, (c) calcium nitrate, (d) calcium chloride.

5. Find the effect of addition of calcium sulphate solution to solutions of the chlorides of barium, strontium, and calcium (a) in the cold, (b) on boiling.

6. Examine the action of solutions of calcium, strontium, and barium chlorides on a solution of potassium chromate (a) in absence, (b) in presence of acetic acid.

7. Compare the actions of the hydroxides of calcium, strontium, and barium on carbon dioxide.

QUESTIONS ON CHAPTER XXVI.

1. Enumerate the chief sources of the metals of the alkaline earths; state how metallic calcium is isolated, and give an account of its properties.
2. How is lime manufactured? Describe its action on (a) water, (b) chlorine, (c) hydrochloric acid.
3. Give an account of the formation of mortar, cement, and plaster of Paris; state their uses.
4. Describe fully the action of carbonic acid on lime-water and on baryta water.
5. What is the action of water vapour, ammonia, and hydrogen sulphide gases on calcium chloride? What gases may be dried by passing them over calcium chloride?
6. Explain the processes by which the phosphorus of an igneous rock may ultimately find its way into the human body.
7. Compare the properties of the elements and compounds of the metals of the alkaline earths. Compare also the compounds of calcium with those of magnesium.
8. Give as many distinguishing tests as you can for the metals of this group.

CHAPTER XXVII

MAGNESIUM, ZINC, AND MERCURY

Magnesium. This element is widely distributed and abundant, though never found uncombined. It occurs as carbonate in magnesite, as double carbonate with calcium in dolomite, as sulphate, called Epsom salt, and as chloride in mineral springs and sea-water; also as silicate associated with other minerals in various rocks. The double chloride, $\text{MgCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$, carnallite, occurs in Germany.

Preparation. Magnesium is prepared by electrolysis of the fused double chloride of magnesium and potassium, which has a lower melting-point than the pure chloride. Magnesium is set free at the kathode and chlorine at the anode.

Properties. Magnesium is a white metal, tough and of low density. The alloy with aluminium (magnalium), owing to its strength and lightness, is used for the beams of chemical balances, &c. It is oxidized slowly on exposure to air and decomposes water slowly at 100°C ., and with incandescence at a red heat (see p. 164). It is quickly dissolved by dilute acids with evolution of hydrogen.

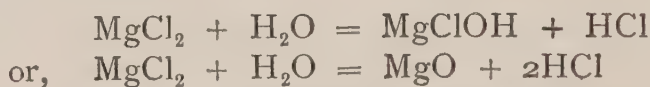
Owing to the great energy with which it combines with oxygen it may be used for reducing refractory oxides, such as those of silicon, boron, and calcium. A heated mixture of pure lime with magnesium dust is used for absorbing nitrogen from atmospheric nitrogen in the preparation of argon (see p. 115).

Magnesium is divalent in all its compounds.

Magnesium hydroxide is precipitated by addition of sodium hydroxide to a solution of a magnesium salt, and is a white powder alkaline to litmus. It is soluble in a solution of ammonium chloride, hence the presence of the latter prevents precipitation of magnesium hydroxide.

Magnesium oxide, MgO , is obtained by decomposing the carbonate by heat. It is a white, very infusible powder, practically insoluble in water. When strongly heated it becomes incandescent, and the intense luminosity of burning magnesium depends on this property. It is used for making crucibles required to withstand a very high temperature.

Magnesium chloride, MgCl_2 . A solution may be made by dissolving the carbonate in hydrochloric acid. On evaporation, however, it loses hydrogen chloride, and either a basic chloride or the oxide is left, according to the degree to which it has been heated.



A method for the manufacture of hydrochloric acid is based on this reaction, natural magnesium chloride being heated in a current of steam.

In order to obtain the pure chloride, ammonium chloride must be added to the solution before evaporation; a stable double chloride is thus formed which can be freed from water by heat. On strongly heating the anhydrous double chloride ($\text{MgCl}_2 \cdot 2\text{NH}_4\text{Cl}$) the ammonium chloride is expelled and pure magnesium chloride, MgCl_2 , results.

Magnesium sulphate, MgSO_4 , called *Epsom salt*, from its presence in the mineral springs at Epsom, is commonly crystallized with seven molecules of water. It may be prepared from the metal, the oxide, or the carbonate by the action of dilute sulphuric acid. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ forms rhombic crystals, and one molecule of water is replaceable by the sulphates of ammonium or the alkali metals, double salts such as $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

Magnesium carbonate occurring as *magnesite*, MgCO_3 , is difficult to prepare free from hydroxide by artificial means. By adding sodium carbonate to a solution of magnesium sulphate, a gelatinous precipitate of basic carbonate is formed with evolution of carbon dioxide. The composition of the solid varies with the conditions of its formation, and consists of mixtures of carbonate and hydroxide in various proportions.

Magnesium carbonate is much more soluble in presence of carbon dioxide and water than is calcium carbonate, owing to the greater stability of the bicarbonate of the former metal. This fact is utilized in the separation of magnesium carbonate from dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$. The finely powdered mineral is suspended in water and subjected to the action of carbon dioxide under pressure. The solution of magnesium bicarbonate decomposes on reduction of pressure, and is thus separated from the comparatively insoluble calcium carbonate.

Magnesium sulphide, MgS , is formed by direct combination of the elements, and is decomposed by water, giving magnesium hydroxide and hydrogen sulphide.

Detection of magnesium in combination. Magnesium salts are decomposed by strongly heating in air, leaving magnesium oxide, which is incandescent and rendered pink by strongly heating with cobalt nitrate. They give no precipitate with hydrogen sulphide, or, in presence of ammonium chloride, with ammonium hydroxide and hydrogen sulphide, nor with ammonium chloride, ammonium hydroxide, and ammonium carbonate. On addition of 'magnesia mixture', i.e. a solution containing sodium phosphate, ammonium chloride and ammonium hydroxide, a precipitate of $\text{MgNH}_4 \cdot \text{PO}_4$ comes down. This substance is decomposed on heating to redness, giving pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, a form in which magnesium is weighed for the purpose of gravimetric estimation.

Practical problems on magnesium compounds. 1. Place 50 c.c. of dilute hydrochloric acid in a basin and add excess of magnesium carbonate. Warm and filter from the excess of carbonate. Show that the magnesium chloride is decomposed on evaporation of a small quantity of the solution. The greater stability of the chloride on evaporation in presence of ammonium chloride may also be shown.

2. Make a fairly dilute solution of magnesium sulphate containing about 5 grams of salt in 100 c.c. of the solution.

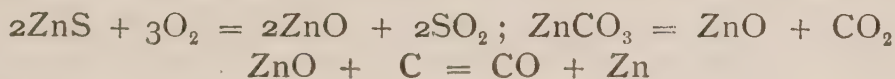
Half fill two test-tubes with this solution, and to one add ammonium chloride solution followed by ammonium hydroxide, and to the other add ammonium hydroxide only. Observe the difference in the results.

3. Mix in a small flask solutions of alum, zinc sulphate, calcium chloride, and magnesium sulphate. Add to the mixture ammonium chloride solution (bench reagent) followed by ammonium hydroxide. Filter. The gelatinous precipitate is aluminium hydroxide. To the filtrate add about 10 c.c. of ammonium sulphide or hydrogen sulphide gas. Filter off the precipitate of zinc sulphide. To the filtrate add a solution of ammonium carbonate, filter and test the precipitate by the flame test, and add a solution of sodium phosphate (Na_2HPO_4) to the filtrate. The precipitate is magnesium ammonium phosphate.

Write chemical equations for the reactions involved in this experiment.

Zinc. This is a fairly abundant metal, but is only found in combination. The ores are zinc sulphide, ZnS , called blende, the carbonate, and the silicate.

Preparation. It is made by reduction of the oxide with carbon, the oxide being obtained by preliminary roasting of the sulphide or carbonate. The metal passes out of the retort as vapour, and is collected in air-cooled condensers.



Properties. Zinc is a white metal, soft and tenacious or hard and brittle, according to its thermal treatment. It melts at 420°C . and boils below 1000°C . In the vapour state the molecules are monatomic.

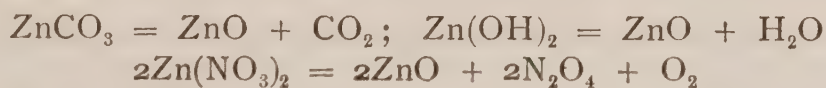
It is not liable to rapid alteration in air, owing to the formation of a protective layer of oxide, and its use as a coating for iron in galvanized iron depends on this fact.

It forms valuable alloys, with copper in brass and with copper and nickel in German silver.

Action of acids. Commercial zinc is readily attacked by even weak acids, hydrogen and the corresponding salt being formed, except with acids such as nitric, which are further reduced by hydrogen. With nitric acid the chief gaseous product is nitrous oxide, N_2O , zinc nitrate and water being simultaneously formed. (See p. 218.)

Zinc forms only one series of compounds, in which it is divalent.

Zinc oxide, ZnO . When zinc is strongly heated in air the vapour burns with a bright blue-green flame, and clouds of zinc oxide (zinc white) are formed. It may also be made by heating the hydroxide, carbonate, or nitrate.



It is a white powder, lemon yellow when hot. It has a very faintly alkaline reaction towards neutral litmus when

moist. Generally it resembles magnesium oxide, but is less strongly basic.

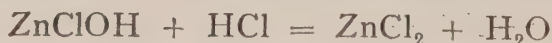
Zinc hydroxide is formed when a soluble hydroxide, such as of sodium or ammonium, is added to a solution of a zinc salt. It comes down as a white gelatinous precipitate. This dissolves on adding an excess either of sodium or ammonium hydroxide. With sodium hydroxide in excess, the zinc goes into solution as sodium zincate, Na_2ZnO_2 . Zinc can therefore act as a very weakly acidic oxide in presence of a strong base such as sodium hydroxide and even in presence of ammonium hydroxide.

Zinc chloride. Zinc is quickly dissolved by hydrochloric acid. On evaporation to dryness *hydrolysis* takes place, i. e. double decomposition between water and the substance, whereby a basic salt (or metallic hydroxide) and free acid are formed. The commercial chloride always contains some basic salt.



Zinc chloride is a white deliquescent solid, which can dissolve large quantities of oxide with formation of basic compounds. Its use as a flux in soldering depends on this property.

Since zinc chloride is volatile it may be freed from basic salt by distillation in a current of hydrogen chloride.



Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, called white vitriol, formed as a by-product in the preparation of hydrogen, has already been examined (p. 180). It is a white crystalline salt, very soluble in water, and when crystallized with $7\text{H}_2\text{O}$ it is isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Zinc carbonate occurring as *calamine*, ZnCO_3 , is a source of the metal. The mineral carbonate is isomorphous with magnesite, MgCO_3 , and calc spar, CaCO_3 . When prepared by precipitation it is generally obtained as a basic carbonate.

Zinc sulphide, ZnS , occurring as *blende*, may be prepared by precipitation of a soluble zinc salt by hydrogen sulphide in presence of an alkali. A neutral solution of zinc sulphate gives a white precipitate of the sulphide on addition of hydrogen sulphide, but it is not complete owing to the formation of sulphuric acid, which causes reversal of the action.



If, however, the salt of a weak acid, such as sodium acetate, is added, the whole of the zinc will be precipitated, zinc sulphide not being soluble in presence of acetic acid.



Practical problems on zinc compounds. 1. Prepare a solution of zinc chloride, using excess of zinc. Boil the solution with a small quantity of zinc oxide, and observe whether the latter dissolves.

2. Fill one-third of each of two test-tubes with a dilute solution of zinc sulphate. To one add ammonium hydroxide and to the other sodium hydroxide solution, a drop at a time and finally in excess. Pass carbon dioxide into the clear solutions; collect and identify the product.

3. Fill one-third of each of three test-tubes (*a*), (*b*), (*c*) with zinc sulphate solution. To (*a*) add saturated hydrogen sulphide solution or the gas; to (*b*) add a few drops of dilute sulphuric acid followed by hydrogen sulphide, and finally some saturated sodium acetate solution; and to (*c*) add ammonium hydroxide until the precipitate of hydroxide is redissolved and then hydrogen sulphide. If a precipitate of zinc sulphide has come down in (*a*) filter and test for the presence of zinc in the filtrate. Explain the observed facts.

4. Make a specimen of the double sulphate $\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in the following manner: Place 50 c.c. of dilute sulphuric acid in each of two basins. Exactly neutralize the first with potassium hydroxide, and add excess of zinc carbonate to the other. When zinc carbonate no longer dissolves, filter the cold liquid and wash, and mix the filtrate and washings with the potassium sulphate. Evaporate to crystallizing point, dry the crystals in air at the ordinary temperature, and determine their percentage of water of crystallization.

Mercury. This metal, so important from its application to scientific purposes, occurs chiefly in the form of sulphide, called *cinnabar*. When the sulphide is roasted in air mercury and sulphur dioxide are formed; the oxide, being unstable, is not found in appreciable quantity. This is the method adopted for the preparation of the metal from cinnabar.



Purification. This is best done by distillation under reduced pressure. Otherwise it may be freed from foreign metals either by shaking with dilute nitric acid or by agitation with a solution of sodium peroxide in water, which oxidizes the more oxidizable metals, but is without action on mercury.

Properties. Mercury is a white liquid metal freezing at -40°C . and boiling at 358°C . Its vapour pressure at air temperature is negligible. Its density is 13.6 g. per c.c. The vapour density of mercury relative to hydrogen is 100, therefore the molecular weight is 200; the A. W. is also 200, hence the molecule only contains one atom. Mercury is unaffected by air at the ordinary temperature, and is not attacked by hydrochloric acid. The best solvent is nitric acid, and it is also attacked by hot concentrated sulphuric acid (see p. 489).

Mercury amalgams. When certain metals, such as zinc or copper, are treated with mercury, they go into solution, an 'amalgam' being formed. Amalgams may also be formed by placing the metal in a solution of a mercury salt or by making mercury the cathode in the electrolysis of a solution of a metallic salt.

Sodium amalgam in presence of water is used as a reducing agent in alkaline solution.

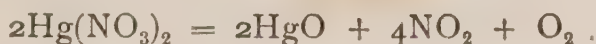
Mercury compounds. Two series of compounds exist, those in which mercury is (1) monovalent, or mercurous compounds, and (2) divalent, or mercuric compounds.

The oxides. Mercurous oxide, Hg_2O , and mercuric oxide, HgO , both exist. They are precipitated by addition of sodium hydroxide to the corresponding mercury salts, the former as a black precipitate and the latter as a bright yellow solid. No hydroxide of mercury is known.

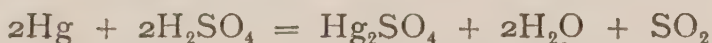
Mercurous oxide quickly changes, on exposure to light, to a mixture of mercury and mercuric oxide.



Mercuric oxide occurs in two forms, the yellow one above mentioned, and the red crystalline form which is obtained when mercury is slowly heated in air, or, better, by carefully heating mercuric nitrate.



Mercurous sulphate is a white crystalline salt made by heating sulphuric acid with excess of mercury.



In presence of water hydrolysis takes place with formation of basic salts by removal of a part of the acid radical as sulphuric acid.

Mercurous chloride, HgCl (calomel), is prepared by double decomposition of a soluble mercurous salt with a soluble chloride. Thus



It is prepared commercially by heating mercurous sulphate with sodium chloride, when the volatile HgCl sublimes. Careful washing with water is necessary to remove the very poisonous mercuric chloride.

Mercurous chloride is a white crystalline powder insoluble in water and acids. Its vapour density shows that the molecule is correctly represented by the formula HgCl .

Mercurous nitrate is obtained by the action of nitric acid with excess of mercury. It is a white, crystalline, soluble salt.

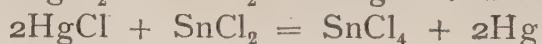
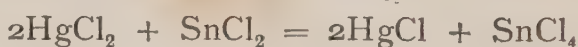


Mercuric salts can be prepared by oxidation of the corresponding mercurous salts, or by the action of the corresponding acid on mercuric oxide.

Mercuric chloride, known as corrosive sublimate, is a white crystalline solid fairly soluble in water. It is very poisonous, and in dilute solution is used as an antiseptic.

It is volatile, boiling at 307°C ., and can be purified by sublimation. The vapour density corresponds to a formula HgCl_2 .

By treatment with reducing agents, such as stannous chloride, it gives the lower chloride, and finally mercury, the white precipitate becoming grey.



This reaction may be used as a test either for mercury or a stannous salt.

Mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, is prepared by acting on mercury with excess of nitric acid. It is a white crystalline solid, which gives basic salts on treatment with water, e.g. :—



It is used for the preparation of red mercuric oxide. Gentle heating brings about the change—



The action of ammonia on mercury salts. Insoluble compounds are precipitated on addition of a solution of ammonium hydroxide to solutions of mercurous or mercuric compounds. These may be regarded as ammonium salts in which two atoms of hydrogen of the NH_4 radical have been replaced by Hg_2 or Hg in mercurous and mercuric compounds respectively. Mercurous chloride is blackened by ammonia, and $\text{NH}_2\text{Hg}_2\cdot\text{Cl}$ is formed, which is called mercurous ammonium chloride. Mercuric chloride gives a white compound, $\text{NH}_2\text{Hg}\cdot\text{Cl}$.

Mercuric sulphide, HgS , when found native as cinnabar, is a bright crimson-red crystalline substance. By precipita-

tion of a mercuric salt with hydrogen sulphide it is obtained as a black powder, which by sublimation gives the red form.

Since mercuric sulphide is not attacked either by hydrochloric or nitric acids, mercury can be separated from metals whose sulphides are precipitated with it by treating the washed mass with nitric acid and water. Mercuric sulphide alone remains undissolved.

Practical Problems on mercury compounds.

Precaution. All mercury compounds are *very poisonous*.

1. Treat a few drops of mercury with equal volumes of nitric acid and water—warm till the metal is dissolved.

Test whether mercurous nitrate is present by adding excess of sodium hydroxide to a *few drops* of the solution. If the dark-coloured mercurous oxide is precipitated add more nitric acid to the nitrate solution. Evaporate to dryness on a sand bath, and ignite gently to obtain the oxide.

2. Dissolve mercuric oxide in hydrochloric acid; evaporate to crystallizing point. Dry the product. What is it?

3. Boil mercuric nitrate with a few drops of mercury. Add hydrochloric acid to half the solution obtained; to the other half add a solution of stannous chloride. Collect and name the solid products.

4. To a solution of mercuric chloride add, a drop at a time, a solution of potassium iodide. Then add excess.

The soluble double mercury potassium iodide, K_2HgI_4 , is formed, which, when made alkaline with potash, is called Nessler's solution.

Add excess of potash to the iodide, and then a drop of ammonia solution or an ammonium salt. This forms a delicate test for ammonia.

5. Obtain a specimen of mercuric sulphide by precipitation of a mercuric solution with hydrogen sulphide; filter and wash the precipitate, and warm a small portion with nitric acid and water 1 : 3. Dry the rest and sublime by heating gently in a test-tube.

6. Make a specimen of mercurous oxide and expose to sunlight. Determine whether the change $Hg_2O = HgO + Hg$ takes place.

7. Mix equal volumes of ammonium oxalate and mercuric chloride of equivalent strength [ammonium oxalate is $(NH_4)_2C_2O_4 \cdot 2H_2O$].

[Over.

Devise a means of collecting any gas which may be given off when exposed to sunlight, and determine the nature of the gas, and also whether the solid which is formed is a mercuric or a mercurous compound.

8. Examine the action of strong solution of sodium chloride on yellow mercuric oxide.

9. Heat a solution of mercuric chloride with yellow mercuric oxide. What is the nature of the substance obtained?

10. Examine the action of excess of water on (*a*) mercuric nitrate, (*b*) mercuric sulphate.

Chemical relationships of magnesium, zinc, and mercury.

Magnesium resembles zinc in some respects and calcium in others. Thus both magnesium and zinc form soluble sulphates, hydroxides which easily lose water, and the metals do not rust rapidly in air nor decompose water at low temperatures. In these points they differ from the calcium group, but magnesium differs from zinc and resembles calcium in the fact that its oxide is not reduced by heating with carbon, and that its sulphide is hydrolysed by water. Magnesium hydroxide is basic, while zinc hydroxide is acidic as well as basic, forming zincates.

Magnesium and zinc only form one series of compounds each, viz. a divalent series, while mercury also forms a univalent series. Mercury has analogies to the noble metals (Cu, Ag, Au), e.g. the low temperature of the decomposition of its oxide. The mercurous halides, like the cuprous and the argentic, are insoluble in water and are decomposed by light. No carbonate of mercury is known.

QUESTIONS ON CHAPTER XXVII.

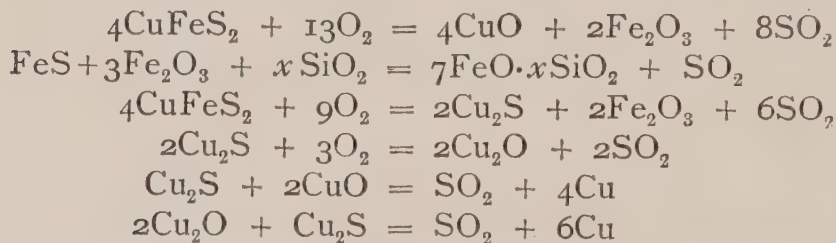
1. Give an account of the preparation and properties of magnesium. How does it react with carbon dioxide, steam, and sulphuric acid?
2. How is anhydrous magnesium chloride made? Explain what happens when its solution is evaporated to dryness.
3. How is magnesium carbonate separated from dolomite?
4. Compare the chemistry of magnesium and its compounds with those of zinc and calcium. How may the oxides of these three metals be distinguished?
5. Describe the principle of the extraction of zinc from blende, and enumerate the chief physical and chemical properties of the metal.
6. Write a general account of the preparation and properties of the chief compounds of zinc.
7. How would you obtain pure mercury from metal contaminated with zinc and copper?
8. Explain the reactions which take place in the preparation of mercury from cinnabar.
9. Suggest a method for determining the equivalent weight of mercury. Mention any special precautions necessary.
10. Describe the preparation of mercuric chloride from mercury. How would you get from it (a) mercurous chloride, (b) mercuric oxide, (c) metallic mercury? Write equations for the reactions.
11. Compare the properties of the chlorides and oxides of mercury with those of copper.
12. How may mercury be separated from other metals whose sulphides are insoluble in dilute hydrochloric acid?
13. Give examples of basic salts of mercury, and shortly describe how you would make a basic chloride of this metal.

CHAPTER XXVIII

COPPER AND ITS COMPOUNDS

Sources. Copper occurs sparingly in the metallic state; its chief ore is the double sulphide with iron, known as copper pyrites, CuFeS_2 . Other ores are malachite and azurite, both of them basic carbonates.

Extraction. The treatment of copper pyrites to extract the copper involves complex processes, of which only an outline can be given here. The ores, containing chiefly copper pyrites and silica, are roasted to cause partial oxidation of the sulphides to oxides, with loss of sulphur dioxide. The iron oxide gives a fusible slag of ferrous silicate when the temperature is raised, and the copper oxide reacts with the iron sulphide, giving copper sulphide and iron oxide. The latter gives more slag by the action of the silica. Eventually copper separates as a nearly pure sulphide, Cu_2S , and on subjection to a roasting process is partly converted to cuprous oxide, Cu_2O , the latter reacting with cuprous sulphide, giving copper and sulphur dioxide. Some of the reactions which take place are as follows:—

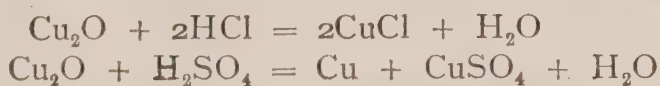


In order to remove the last traces of oxide, the molten copper is covered with pure powdered charcoal and stirred with a pole of green wood. The reducing gases set free convert the copper oxide to copper.

Properties. Copper is a bright rose-red metal melting at about 1000°C . After silver, it is the best conductor of heat and electricity. It is tarnished slowly in air, partly owing to the action of sulphur compounds, which form a film of sulphide. It is not readily attacked by acids, except by nitric (see p. 399). Its alloys in common use are: *brass*, containing copper and zinc; *bronze*, copper and tin; *German silver*, copper, nickel, and a little zinc; and *gun-metal*, composed of copper and tin.

Copper forms two series of compounds, in one of which it is monovalent, in the other divalent.

The oxides and hydroxides of copper. *Cuprous oxide*, Cu_2O , is prepared by the action of certain reducing agents on a hot alkaline solution of a cupric salt. When cupric hydroxide is warmed with an alkaline solution of sodium tartrate, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, it dissolves, and the deep-blue liquid is known as Fehling's solution. On the addition of grape sugar to Fehling's solution and boiling, a crimson precipitate of cuprous oxide is formed. Cuprous oxide is difficult to prepare free from copper, and on heating in air it is quickly oxidized to the cupric form. It gives cuprous chloride with hydrochloric acid, but sulphuric acid gives copper and cupric sulphate.



Cupric oxide, CuO , is a black powder, or grey and crystalline. It is quite insoluble in water, but quickly reacts with acids, giving a salt and water. At very high temperatures it loses oxygen, forming cuprous oxide. Cupric oxide has very weakly acidic properties, shown by its slight solubility in concentrated sodium hydroxide.

Cupric hydroxide, $\text{Cu}(\text{OH})_2$, is the blue precipitate formed when an alkaline hydroxide is added to a solution of a copper salt. It is a very unstable substance, quickly losing water when heated, with formation of black copper oxide.

Salts of copper. The weakly basic character of copper hinders the formation of cupric compounds with weak acidic radicals or of cuprous compounds with strong acidic radicals. Thus, while cupric chloride and bromide are fairly stable salts, the corresponding cupric iodide, at the moment of its formation, splits up into iodine and cuprous iodide.

Similarly, in reactions in which the formation of cuprous sulphate might be expected, cupric sulphate is formed with separation of copper.



Cuprous chloride, CuCl , is formed when cupric chloride is boiled with copper and hydrochloric acid. It may also be formed by passing sulphur dioxide into a saturated solution of copper sulphate and sodium chloride. In either case the cuprous chloride can be separated from the solution by dilution, since it is insoluble in water.

It is a white solid, crystallizing in cubes and insoluble in water, but soluble in a solution of sodium chloride or hydrochloric acid. The solution in hydrochloric acid contains the acid H_2CuCl_3 . When moist it is quickly oxidized, especially in presence of hydrochloric acid.



Cuprous chloride is soluble in ammonium hydroxide, and the solution in presence of acetylene gives a bright red compound, $\text{C}_2\text{H}_2\text{Cu}_2\text{O}$.

Cuprous chloride is volatile without decomposition, and the vapour density shows the formula of the compound to be CuCl .

Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, prepared by the usual methods, is a bright green crystalline solid, very soluble in water, forming, when dilute, a blue liquid. When heated, it loses its water of crystallization, giving a brown anhydrous

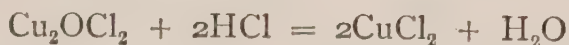
salt (see p. 190); on further heating it melts and loses chlorine, with formation of cuprous chloride.



When heated in presence of air an oxychloride is formed, the production of which forms the basis of *Deacon's process* for the preparation of chlorine. A mixture of hydrogen chloride and air is passed over hot brick previously soaked in copper sulphate. Cupric chloride is formed, and in presence of oxygen it loses chlorine, and the oxychloride, Cu_2OCl_2 , is formed,



In presence of hydrochloric acid the following reaction takes place:—



The same reactions take place over and over again, the cupric chloride acting as an oxygen carrier to the hydrogen chloride.

When cupric oxide is boiled with a solution of cupric chloride a green basic chloride is formed.

Cupric chloride dissolves in hydrochloric acid, giving a deep brown-yellow solution. Since salts of the type K_2CuCl_4 are known, the acid solution may be supposed to contain the unstable acid, H_2CuCl_4 .

Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This is the commonest salt of copper, and is known as blue vitriol (see p. 196). Since copper is not attacked by dilute sulphuric acid, it is made from the oxide and sulphuric acid. When the crystals are heated they lose water, giving successively the hydrates with three and one molecule of water, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

Cupric nitrate, $\text{Cu}(\text{NO}_3)_2$. This is a blue salt formed most conveniently by the action of nitric acid on copper (see p. 399). It is deliquescent and very soluble in water,

giving a strongly acid solution. Heat causes decomposition thus :—



Like other copper salts, it readily forms basic salts with loss of acid.

Copper carbonate. Basic carbonates only are obtainable, the natural form, malachite, being



Azurite is also a basic compound.

When a solution of sodium carbonate is added to a solution of copper sulphate, a blue solid is first formed, which quickly begins to lose carbon dioxide, and a green basic carbonate having the same composition as malachite remains.



The sulphides of copper. *Cuprous sulphide*, Cu_2S , is formed when cupric sulphide is heated (see p. 244).



It is a dark blue-black solid. When heated in air it loses sulphur, giving cuprous or cupric oxide.

Cupric sulphide, CuS , is formed when hydrogen sulphide is passed into a solution of a cupric salt. It is decomposed when heated below redness. (Compare the stability of the two oxides with that of the sulphides.) Copper sulphide is easily oxidized by dilute nitric acid.



The tests for copper. The compounds of copper are reduced fairly easily on charcoal, and, in presence of a flux such as sodium carbonate, which protects the metal from the air, may be recognized by the red colour of the mass and by its malleability. In solution, cupric compounds are blue, and give a blue precipitate of hydroxide with sodium hydroxide, which gives black copper oxide on heating. Ammonia forms intensely blue-coloured compounds with cupric salts.

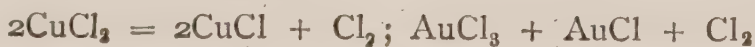
The relationships of copper. This element occurs in the same group as silver and gold (see table, p. 317), but these three elements do not show many points of similarity. Copper and gold form two series of salts; those of the former are monovalent and divalent, and of the latter monovalent and trivalent. Combined silver is only known in monovalent form.

The oxides of silver and gold are decomposed by heat, whilst those of copper are stable towards heat. Auric oxide is acidic, whilst cupric oxide only shows the weakest possible acidic character by dissolving in strong caustic soda, giving a blue solution.

Cuprous chloride and silver chloride, AgCl , are insoluble in water, whilst aurous chloride is decomposed on treatment with water into gold and auric chloride.



Cupric and auric chlorides are decomposed by heat in a somewhat similar manner.



The isomorphism (i. e. identity of crystalline form) of cuprous and silver chlorides with the chlorides of the alkali metals is an indication of relationship.

Generally considered, the basic character in this group decreases with increasing atomic weight.

Practical Problems.

[Devise a detailed method for each problem, and submit it for inspection before starting.]

1. Starting with copper turnings, prepare 5 g. of crystalline copper nitrate.
2. Prepare 3 g. of the basic carbonate of copper, starting with a solution of the nitrate.
3. Obtain cupric oxide from (a) the nitrate, (b) the carbonate. Test each specimen for free copper.
4. Given cupric oxide, obtain specimens of (a) cupric, (b) cuprous chlorides.

5. Make a small quantity of cuprous oxide from a solution of a cupric salt.
6. From a soluble cupric salt make some cupric sulphide. Use part of this to obtain cuprous sulphide.
7. Precipitate some cupric hydroxide from copper sulphate solution, and observe the action of heat on it while suspended in the liquid.
8. Observe the action of solutions of (a) ammonium hydroxide, (b) potassium ferro-cyanide, on a solution of any cupric salt. Also the effect of placing pieces of bright iron wire into a solution of a copper salt.

QUESTIONS ON CHAPTER XXVIII.

1. What are the chief ores of copper? Write an outline of the extraction of the metal.
2. Starting with copper turnings, give details for the preparation of the following compounds of copper: Cuprous oxide, cupric acetate, cuprous chloride, cupric chloride.
3. Write equations for the following reactions: (a) the action of heat on copper nitrate; (b) sulphuric acid on cuprous oxide and (c) on cuprous chloride; (d) copper sulphate on potassium iodide; (e) the action of heat on cupric chloride in presence and absence of air; (f) the reactions which take place when a solution of copper sulphate is electrolysed.
4. How would you prepare basic sulphate of copper, $\text{CuO} \cdot \text{CuSO}_4$?
5. Describe a method by which the weight of copper sulphate present in 1 litre of a solution might be ascertained.
6. By what tests may copper be recognized? Describe several.

CHAPTER XXIX

ALUMINIUM AND ITS COMPOUNDS

Aluminium is found in a variety of minerals; some of the more important are—aluminium oxide, Al_2O_3 , which occurs as emery, ruby, and sapphire; a double oxide of aluminium and iron called bauxite; cryolite or sodium aluminium fluoride; and a great variety of silicates, of which potash felspar, $\text{K}_2\text{Al}_2\text{SiO}_6$, may be mentioned. Clay is a hydrated aluminium silicate formed by the weathering of felspar.

Preparation. Although the most abundant of all the metals, it is only recently that economical methods of extraction have been invented. Where electrical power is cheap it is made by the electrolysis of a mixture of aluminium oxide with cryolite, the presence of the latter substance causing fusion and solution of the aluminium oxide. The reaction is carried out in iron vessels lined with fireclay, and inside this a lining of gas carbon. The bottom of the crucible is prolonged to a cone-shaped exit closed by a plug. The lining of the crucible is made the kathode, and the anode consists of thick carbon rods. The products of the electrolysis are aluminium and oxygen, and the latter combines with the anode and escapes as carbon monoxide, whilst the aluminium falls to the bottom and is from time to time removed by pushing in the plug.

Properties. Aluminium is a very light metal of sp. g. 2.7, white, with a silvery lustre, and is almost unchanged in air. It is slowly attacked by water at 100°C ., and the finely divided metal decomposes steam at a red heat, with incandescence.

By solution of aluminium in mercury the oxidation of the former by moist air is rendered very rapid. It is mainly a decomposition of the water by the finely divided aluminium, hydrogen and the hydroxide being formed. Hence aluminium amalgam is a powerful reducing agent in presence of water, nitrates being rapidly converted to ammonia.

The metal and its alloys, magnalium and aluminium bronze, are used for making cooking utensils, fittings for cameras, opera glasses, &c. Aluminium paint is a mixture of the powdered metal with oil.

The action of acids. Nitric acid is almost inactive towards aluminium, owing to the immediate formation of a protective layer of oxide.

Hydrochloric acid, both diluted and otherwise, quickly dissolves the metal, with formation of the chloride and hydrogen. Diluted sulphuric acid reacts rapidly, leaving a solution of the sulphate.

Aluminium oxide, Al_2O_3 . Only one oxide is known, and is prepared by decomposition of the hydroxide by heat or by the action of carbon dioxide on sodium aluminate.

It is a white infusible solid, insoluble in acids, but dissolved by fusion with alkalis, with formation of aluminates.



Aluminium hydroxide behaves similarly towards alkalis, and thus acts both as a weakly basic oxide towards acids, and an acidic oxide towards bases.

The weakly acidic character is shown by the action of carbon dioxide.



Aluminium hydroxide, $\text{Al}_2(\text{OH})_6$, is formed by addition of ammonium hydroxide or sodium hydroxide to any soluble aluminium salt. It is a white gelatinous solid, insoluble in ammonium hydroxide, but soluble in sodium hydroxide (forming sodium aluminate), and also in hydrochloric and sulphuric acids, forming the chloride and sulphate.

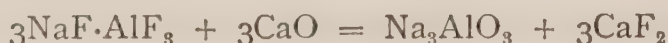
When precipitated in presence of colouring matter such as litmus, the colouring matter comes down with the hydroxide, forming a *lake*. Aluminium salts are therefore used as *mordants* for steeping tissues to be dyed, since the aluminium hydroxide, always present owing to partial hydrolysis of the salt, attaches itself firmly to the fibre and holds the colouring matter.

Aluminium chloride, AlCl_3 , is formed by direct union of the elements, and owing to its being volatilized below 200°C . can be readily obtained pure.

It is a white solid very soluble in water. The solution has a strongly acid reaction, and on evaporation the chloride is completely decomposed to aluminium oxide and hydrochloric acid.

Its vapour density becomes constant above 450°C ., and corresponds to a formula AlCl_3 , showing aluminium to be trivalent.

Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, is made by the action of sulphuric acid on aluminium oxide. Commercially it is now made from cryolite, $3\text{NaF}\cdot\text{AlF}_3$, by fusion with lime, whereby calcium fluoride and sodium aluminate are formed.



The aluminate is dissolved out by water and decomposed by carbon dioxide.



Sodium carbonate is thus formed as a by-product. The aluminium oxide is dissolved by dilute sulphuric acid.

It is a white crystalline solid containing 18 molecules of water of crystallization.

Alum. When solutions of the sulphates of aluminium and potassium are mixed and allowed to crystallize, colourless octahedral crystals are obtained, having a composition expressed by the formula $\text{K}_2\text{SO}_4\cdot\text{Al}_2(\text{SO}_4)_3\cdot 24\text{H}_2\text{O}$.

Double salts of this type are called alums. Potassium may

be replaced by ammonium, silver, caesium, rubidium, or sodium, whilst ferric iron, manganese, chromium, gallium, thallium, all of them trivalent, may replace aluminium.

The replacement of potassium and aluminium by other radicals to form mixed crystals is a good example of isomorphism.

Isomorphous elements are those which can replace one another in their compounds in any proportions to form mixed crystals having the same crystalline form.

Thus silver will replace potassium wholly or partly in ordinary alum, and, providing that the total weights of silver and potassium is equivalent to the sulphate radical, the proportions of these two metals may vary indefinitely.

Since potassium is isomorphous with silver, the sulphates of these two metals can never be separated by fractional crystallization.

Porcelain, earthenware, &c. *Porcelain* is made from china clay, a very pure form of hydrated aluminium silicate. The clay is moulded and then dipped into a milk prepared from finely ground felspar and water.

When fired the felspar melts and permeates the clay, forming a highly glazed translucent mass.

Earthenware is made from clay. It is baked and glazed by throwing salt into the furnace. The sodium gives a fusible sodium aluminium silicate with the clay, and hydrochloric acid escapes.

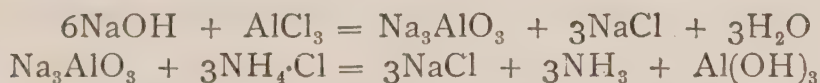
Brick is clay, containing more or less iron, which has been moulded and baked. The water is driven off, and if much iron is present the brick will have a dark red colour owing to the presence of ferric oxide. White bricks are made from clay which is practically free from iron.

Detection of aluminium. When aluminium compounds are strongly heated the mass is incandescent, and leaves a blue residue when heated strongly with cobalt oxide.

Aluminium in solution gives a gelatinous precipitate of hydroxide with ammonium hydroxide.

If sodium hydroxide is added to a solution of an aluminium salt the hydroxide is precipitated, but is redissolved on adding more caustic soda.

Ammonium chloride re-precipitates the hydroxide by decomposing the aluminate.



Chemical relations of aluminium. The other elements in this group are rare. The hydroxide of aluminium is less basic than bivalent hydroxides, such as that of zinc, $\text{Zn}(\text{OH})_2$. They resemble one another in being feebly acidic as well as basic; thus aluminium forms two types of compounds, $\text{Na}_3\cdot\text{AlO}_3$, in which it is acidic, and $\text{Al}_2(\text{SO}_4)_3$, in which the metal is basic. Both types are hydrolysed by water, i. e. they enter into double decomposition with water.

Practical Problems. 1. Heat a fragment of aluminium foil in air, and **note** whether it is oxidized or not.

2. Observe the action of hydrochloric, nitric, and sulphuric acids, dilute and concentrated, on fragments of the metal.

3. Examine the action of sodium hydroxide solution on the metal. When all action has stopped, pass a stream of carbon dioxide into the solution until there is no further change. Describe and explain the actions.

4. Place some mercury on a strip of recently cleaned aluminium foil. Rub the mercury on to the foil strongly, whereby the two metals are caused to alloy. Divide the strip into two parts; place one piece in a basin of water and invert a test-tube of water over it, and leave the other in a dry basin. Observe the action in each case from time to time. Find out whether the solid which forms on the dry aluminium is hydroxide or oxide by gently heating in a bulb tube.

5. Perform the tests given on pp. 504, 505 with ordinary alum (potash alum).

6. Prepare crystalline specimens of potash alum and chrome alum, starting with the sulphates of each metal.

QUESTIONS ON CHAPTER XXIX.

1. Name the chief sources of aluminium, and explain how the metal is extracted.
2. Describe the physical properties and chemical reactions of aluminium; mention the uses of the metal.
3. Describe experiments to show that the oxide of aluminium is both basic and acidic.
4. Explain the terms—hydrolysis, lake, mordant, and illustrate them by reference to aluminium compounds.
5. What is an alum? Explain how iron alum can be made.
6. Give an account of the composition of porcelain, earthenware, and brick.
7. How may aluminium compounds be distinguished from magnesium compounds?

CHAPTER XXX

TIN, LEAD, AND THEIR COMPOUNDS

Tin. *Sources and extraction.* Tin dioxide, or *tinestone*, SnO_2 , is the common ore of this metal. It is always associated with arsenic and iron tungstate, FeWO_4 .

In smelting tin ores the arsenic is removed as volatile arsenious oxide, As_4O_6 , by roasting in air.

To remove tungsten, the presence of which spoils the tin, the roasted ore is heated with sodium carbonate and the mass washed with water. Soluble sodium tungstate, Na_2WO_4 , is removed, and the iron remains as iron oxide. The treated ore is now mixed with anthracite, a pure form of coal, and heated in a furnace, whereby tin containing some iron, and carbon monoxide, is produced. The tin is purified by melting on an inclined plane, when pure tin runs off, leaving behind a less fusible alloy of tin and iron. It is further purified by stirring when in a molten state with a pole of green wood. The reducing gases from the wood remove the last traces of oxide.

Properties. Pure tin is a white metal melting at 227°C . and having a density of 7.3, nearly the same as zinc. It usually has a crystalline structure, and is rather a bad conductor of heat and electricity. It forms a number of important alloys: *pewter* and *solder* contain tin and lead, *britannia* and *white metal* contain tin, lead, and antimony, whilst *gun-metal* is composed of tin and copper.

Tin can exist in two forms, white and grey, the latter being formed from white tin by prolonged exposure to a low temperature.

Action with acids. Hydrochloric acid acts slowly, giving hydrogen and stannous chloride, SnCl_2 . Hot sulphuric acid gives stannous sulphate (SnSO_4), sulphur dioxide, and water.

Nitric acid acts readily with tin, giving products the nature of which depends on the temperature and degree of dilution of the acid.

Tin forms two series of salts, stannous and stannic, in which it acts respectively as a divalent and tetravalent metal, the corresponding oxides being SnO and SnO_2 .

Exp. I. To examine the action of tin with nitric acid.

A. Put fragments of granulated tin in a small flask and fill the flask with carbon dioxide so as to exclude the air. Cover the metal with cold nitric acid diluted 1:4 with water. Cork tightly and set aside whilst carrying out *B*.

B. Pour a few drops of concentrated nitric acid on to fragments of tin contained in a basin. Place the basin on a sand bath in a *draught-chamber* and heat till all action has ceased and fumes no longer escape.

Examine the tin dioxide and test its solubility in nitric and hydrochloric acids.

Now examine the liquid in *A*. Put a portion in a test-tube and boil. To another portion add sodium hydroxide in defect and then in excess and boil. **Note** whether ammonia is set free and any other changes take place.

When concentrated nitric acid acts on tin, stannic nitrate is not formed except as an intermediate stage, since it would be immediately hydrolysed by water thus:—



Stannic hydroxide loses water, giving H_2SnO_3 , stannic acid, or usually the still less hydrated metastannic acid, $\text{H}_2\text{Sn}_5\text{O}_{11}$ ($\text{H}_2\text{O} \cdot 5\text{SnO}_2$).

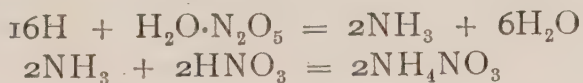
The white solid left from *B* is the latter compound, and gives pure tin dioxide with loss of water on strongly heating.

With diluted nitric acid in the absence of air stannous oxide, a black substance, is usually formed, together with some stannous nitrate, ammonium nitrate, and water.

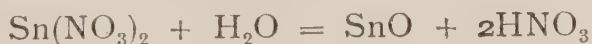
The following equations show the probable course of the change:—



The hydrogen at the moment of its release acts on nitric acid and gives ammonia, which combines with nitric acid, with formation of ammonium nitrate.



Some of the stannous nitrate is hydrolysed by the water, giving stannous oxide and nitric acid.



Oxides of tin. The action of concentrated nitric acid on the metal, as described above, followed by heating the product, is the usual way of preparing *stannic oxide*. By weighing the tin taken and the oxide produced, the figures necessary for the calculation of the E.W. of tin are obtained.

Stannic oxide is a white powder which turns yellow on heating, but turns white again on cooling, like zinc oxide. After strong ignition it has very little action on acids, but when made at a low temperature it interacts easily. It is reduced to the metal when heated in a current of hydrogen.

Stannous oxide, SnO , is made by heating stannous oxalate in absence of air.



It is a black powder which combines with oxygen when heated in air, forming the dioxide, SnO_2 .

The only important salts are stannous sulphate and stannous chloride.

Exp. 2. To prepare and examine stannous chloride and stannous sulphate.

A. Cover some fragments of tin in a basin with concentrated hydrochloric acid. Heat gently over gauze in the draught until action ceases. Pour off the liquid into another basin and evaporate on a steam-bath to crystallizing point.

Dissolve a small portion of the stannous chloride in water in a test-tube, and add sodium hydroxide. Boil the liquid. **Note** the result.

To another portion of the solution in water add a solution of mercuric chloride. The changes which take place are due to the strong reducing power of stannous chloride. The white precipitate which first appears is mercurous chloride, HgCl , which is further reduced to mercury.

B. Warm some tin with concentrated sulphuric acid in a test-tube, and identify the gas which is set free.

Questions :—(i) Write equations for the action of hydrochloric and sulphuric acids on tin.

(ii) What is formed when sodium hydroxide is added to stannous chloride and then the solution is boiled? Write equations for the changes.

(iii) Make out equations for the reduction of mercuric chloride first to mercurous chloride and then to mercury by the action of stannous chloride.

Stannic chloride, SnCl_4 , is formed when chlorine is passed over metallic tin. The arrangement shown in Fig. 91, p. 412, may be used.

The chlorine is dried by passage through sulphuric acid, and the stannic chloride is distilled off from the retort into a receiver.

It is a strongly fuming liquid boiling at 114°C . It combines readily with water, forming a hydrate, sometimes called butter of tin, and with a large excess of water it is

hydrolysed, with formation of stannic acid, H_2SnO_3 . Stannic chloride behaves therefore as an acid chloride.



The same substance is also formed when ammonium hydroxide is added to a solution of stannic chloride.



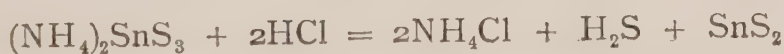
When solutions of stannic chloride and the chlorides of the alkali metals are mixed and evaporated, double chlorides are obtained, which may be regarded as derived from an acid, H_2SnCl_6 . The best-known salt of this type is $2\text{NH}_4\text{Cl} \cdot \text{SnCl}_4$ or $(\text{NH}_4)_2\text{SnCl}_6$, used in dyeing, and known as 'pink salt'.

Sulphides of tin. Stannous and stannic sulphide, SnS and SnS_2 , are formed when hydrogen sulphide is passed into solutions of stannous and stannic salts respectively.

Stannous sulphide, SnS , is a dark brown solid, soluble in ammonium sulphide, giving a solution of ammonium thio-stannate.



When the solution is acidified stannic sulphide is precipitated.



Stannous sulphide is soluble in hydrochloric acid, hydrogen sulphide and stannous chloride being formed.

Stannic sulphide, SnS_2 , comes down as a dirty yellow precipitate when hydrogen sulphide is passed into an acid solution of a stannic salt.

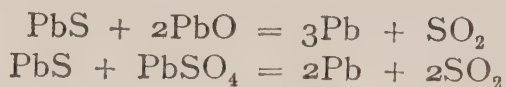
It is soluble in ammonium sulphide, $(\text{NH}_4)_2\text{S}$, giving the same compound as does stannous sulphide, namely thio-stannate, $(\text{NH}_4)_2\text{SnS}_3$.

Stannous and stannic compounds are detected by their behaviour with hydrogen sulphide in dilute hydrochloric acid solution.

Chemical relations of tin. From a study of the compounds of tin we see that they have a markedly non-metallic character. This is especially so in the case of the stannic compounds. Thus stannic oxide hardly functions as a basic oxide at all, the chloride is decomposed by water, and the sulphide has a weakly developed acid character as shown by the formation of thiostannates, tin appearing in the acid radical in these compounds. Stannous oxide is more basic, and forms a stable chloride, sulphate, and nitrate, but it is also feebly acidic, as shown in the formation of sodium stannite, Na_2SnO_2 , by the action of sodium hydroxide on stannous hydroxide.

Lead. Sources and extraction. The chief ore of lead is the sulphide, PbS , called galena. It is found in veins associated with quartz, fluor-spar, barytes, and other minerals.

When heated in an oxidizing atmosphere, it is partly converted to lead oxide and some also to lead sulphate. When the mixture of lead oxide and sulphide is more strongly heated, metallic lead appears and sulphur dioxide escapes. Similarly lead sulphide and sulphate react, giving lead and sulphur dioxide.



Lead, when first smelted, always contains some silver. This is extracted by making use of the fact that pure lead has a higher melting-point than its alloy with silver. The lead is melted and allowed to cool slowly, when pure lead crystals fall to the bottom and are removed from time to time by means of perforated ladles. By such treatment the percentage of silver is raised until the value of the lead still present becomes negligible. The metal is then cupelled. The rich lead is placed in shallow crucibles, called cupels, lined with bone ash, a very porous material, and an oxidizing flame is directed on to the surface of the metal. The lead is converted to lead oxide, and, soaking into the surface of the cupel, leaves behind a button of metallic silver.

Exp. 3. To show the formation of lead oxide by roasting powdered galena.

Use a draught-tube (p. 428) and place some finely powdered galena in the short limb. Heat strongly and **note** whether (a) lead oxide, (b) sulphur dioxide are formed.

The properties of lead. Lead is a heavy blue-white metal, soft and fairly malleable. It melts at 325°C. , and is a bad conductor of heat and electricity. A film of oxide soon forms on a bright surface, which protects the metal from further action. The molten metal quickly takes up oxygen, giving the monoxide called litharge.

Action of water. In water containing dissolved air lead hydroxide is formed. This is slightly soluble in pure soft water or water containing ammonium salts. If carbon dioxide or calcium bicarbonate are present in the water, the hydroxide is converted into the basic carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, which is quite insoluble. Hence a water containing calcium bicarbonate is less likely to produce lead poisoning than pure water (see p. 352).

Action of acids. Strong hydrochloric acid attacks lead slowly when hot, lead chloride and hydrogen being formed.



Diluted sulphuric acid has no action, but the usual reduction of the sulphuric acid takes place if it is hot and concentrated.



Nitric acid, if warm and diluted, gives lead nitrate, oxides of nitrogen, and water. The nitrate is the source of lead compounds in the laboratory.

Exp. 4. To prepare lead nitrate and examine its properties.

Put 10 grams of lead (preferably as foil) in a basin placed in a draught-chamber and cover with nitric acid diluted with twice its volume of water. [Over.

Heat the basin on gauze, with constant stirring until the action slackens. Decant the liquid into another basin and stand it in water to cool. Pour more nitric acid on the lead, again heat and decant. The solution of lead nitrate should crystallize on cooling, and may be obtained almost dry by filtration under pressure. The filtrate will give a second crop on further evaporation.

Examine the crystals and **note** their shape, using a lens if necessary.

Exp. 5. To prepare the chief salts of lead.

A. The haloid salts of lead, PbCl_2 , PbBr_2 , PbI_2 . These may be prepared by double decomposition between lead nitrate and the sodium or potassium salts of the halogen acids.

Into each of three small flasks, *a*, *b*, and *c*, put about 10 c.c. of a solution of lead nitrate.

Add a solution of potassium chloride to (*a*), potassium bromide to (*b*), and potassium iodide to (*c*), until in each case precipitation is complete.

Boil the contents of each of the flasks and add distilled water until the precipitate is in each case dissolved on boiling the liquid.

Allow the flasks to cool slowly and examine the crystals on a slip of glass under a microscope.

B. Lead sulphate, PbSO_4 . Add to about 10 c.c. of lead nitrate solution a few drops of dilute sulphuric acid, avoiding excess of the acid. Filter and add a few drops of methylated (industrial) spirit to half the clear filtrate, and barium nitrate to the other half.

Pierce the filter-paper and wash through into a test-tube with a little ammonium acetate solution. Boil, filter, and test the filtrate for lead with potassium iodide.

C. Basic lead carbonate, $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ (white lead). Add sodium hydroxide to a solution of lead nitrate until

the precipitate which first forms is redissolved. Pass carbon dioxide through the clear liquid until no further precipitation takes place.

Boil and filter the liquid, and wash the lead carbonate with hot water.

Dissolve a little of the solid in acetic acid, and test for a nitrate by means of the ferrous sulphate test (p. 400). Also, test the solid for alkali, and if present the precipitate must be boiled with water and again filtered.

Dry the precipitate at 110°C . in an oven. Examine the action of heat upon it.

D. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, may be prepared by dissolving either lead carbonate or oxide in hot acetic acid. It is commonly known as *sugar of lead*, and is a white crystalline solid not unlike crystallized sugar. It has a sweet taste and is very poisonous, like all soluble lead salts.

E. Lead sulphide, PbS . To a solution of lead nitrate add hydrogen sulphide solution.

Filter the liquid and wash the precipitate of lead sulphide into a small flask. Add a little dilute nitric acid and warm over gauze. When it has all dissolved (except some sulphur), add industrial spirit to a small portion in a test-tube and **observe** the result.

Questions :—(i) Write equations for the formation of each of the lead compounds you have made.

(ii) What is the cause of the action of (a) alcohol, (b) barium nitrate, with the filtrate from lead sulphate?

(iii) The formation of which compound of lead would be the most striking test for the presence of a lead salt in solution?

(iv) Lead hydroxide dissolves in excess of sodium hydroxide, giving sodium plumbite, Na_2PbO_2 . Explain the action of carbon dioxide on the solution, supposing that $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ is formed.

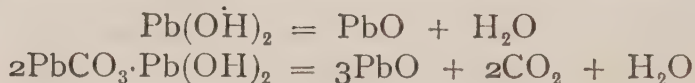
(v) Write an equation for the action of (a) heat, (b) acetic acid ($\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$) on basic lead carbonate.

[Over.

- (vi) What is formed when lead sulphide is warmed with dilute nitric acid?
- (vii) Make out a table showing roughly the order of solubility in water of the compounds of lead which you have prepared.
- (viii) Explain the action of ammonium acetate on lead sulphate, and write out an equation.

The oxides of lead. The most important of the five oxides are the monoxide or litharge, PbO ; red lead, Pb_3O_4 ; and lead dioxide or peroxide, sometimes called puce-coloured oxide of lead, PbO_2 .

Lead monoxide, PbO , is formed when lead is heated in air or oxidized by heating with nitre. It is also formed by the action of heat on the hydroxide or the carbonate.

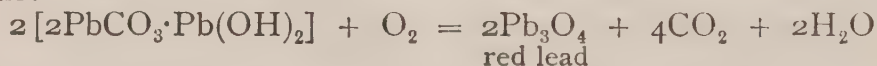


When pure it is a yellow powder having an alkaline reaction in presence of water. In other respects it gives the ordinary reactions of a basic oxide.

Cautious heating in the air causes it to combine with oxygen to form red lead, a method adopted for the preparation of the latter substance.

Exp. 6. To observe the properties of red lead.

This oxide is formed as mentioned above, and also by the carefully regulated action of heat on white lead in presence of air.



(a) Observe the action of heat on some red lead contained in a small ignition tube.

(b) Warm a little red lead in a test-tube with hydrochloric acid, and identify the products.

(c) Warm some red lead with dilute nitric acid in a small flask. Filter, and evaporate the filtrate to crystallizing point. Identify the substance obtained. Wash the solid on the filter paper, and dry in an oven. Keep this substance for the next experiment.

Exp. 7. To prepare lead dioxide and to examine its properties.

This substance has already been prepared by the action of chlorine on lead monoxide in presence of water (p. 294), and was made in the last experiment by the action of nitric acid on red lead. It is best made in quantity by the action of chlorine or a solution of bleaching powder on an alkaline solution of a lead salt.

DIRECTIONS. Grind up some bleaching powder with water in a mortar, and filter. The solution thus obtained contains calcium hydroxide, calcium chloride, and calcium hypochlorite.

Add this solution to some lead nitrate solution, and boil. Let the precipitate settle, pour off the liquid, add more water, boil and again pour off. Now add dilute nitric acid and boil, and, having filtered, wash the precipitate several times with boiling water. Dry the solid in the oven.

Using the lead dioxide prepared in the last experiment, examine the action upon it of (a) heat, (b) hydrochloric acid, (c) sulphuric acid.

Questions on Exps. 6 and 7:—(i) Give equations for the action of heat on red lead and on lead dioxide.

(ii) Red lead may be regarded as a compound of lead monoxide with lead dioxide. Explain the action of nitric acid on red lead.

(iii) Treating lead dioxide as a peroxide, give equations for the action of (a) heat, (b) hydrochloric acid, (c) sulphuric acid, upon it.

Table showing relations of compounds of elements of the carbon group:—

	Carbon.	Silicon.	Germanium.	Tin.	Lead.
Atomic weights	12	28	72	118	207
Atomic volume	→	increasing		→	
M. Point	→	decreasing		→	
Oxides	CO ₂	SiO ₂	GeO	SnO	PbO
	CO ₂		GeO ₂	SnO ₂	PbO ₂
					Pb ₃ O ₄
Chlorides	CCl ₄ , &c.	SiCl ₄	GeCl ₂	SnCl ₂	PbCl ₂
		Si ₂ Cl ₆	GeCl ₄	SnCl ₄	PbCl ₄
					v. unstable
	no salts	no salts	salts	salts	forms salts
			easily hydrolysed		
	electro-negative character decreasing shown by				
	→				
	increasing stability of chlorides towards water				
	and decreasing acidity of oxides.				

QUESTIONS ON CHAPTER XXX.

1. How is tin extracted from tinstone? What actions have the common acids on this metal?
2. How can pure stannic oxide be made from tin? Explain how the E.W. of stannic and stannous tin can be found.
3. What chlorides of tin exist? How are they made, and what are their leading properties?
4. By what tests can stannous and stannic salts be distinguished?
5. Give an account of the extraction of lead from galena, and explain how it is separated from silver.
6. What is the action of lead on water, air, and the common acids?
7. Starting with metallic lead how would you obtain pure specimens of its nitrate, monoxide, chloride, and sulphate?
8. How are red lead and lead peroxide made? Compare their reactions when (a) heated, (b) treated with hydrochloric acid, (c) with nitric acid.
9. Compare the elements lead and tin in light of the periodic system.
10. What is the composition of:—(a) white lead, (b) pewter, (c) litharge, (d) gun-metal, (e) solder, (f) red lead?

CHAPTER XXXI

IRON, NICKEL, AND COBALT

Sources of iron. On account of its abundance, valuable properties, and the comparative ease with which it may be separated from its ores, iron must be regarded as the most important of the metals. Its uses are so universal that the industrial progress of a community may be gauged by the rate of increase of its consumption of iron.

Large masses of metallic iron of meteoric origin, which have fallen on to the earth's surface during her passage through the zones of meteorites in August and November, are occasionally found, but otherwise uncombined iron is rarely found. The common ores are the oxides, haematite, Fe_2O_3 ; magnetite, Fe_3O_4 , with hydrated forms of these. Ferrous carbonate, FeCO_3 , occurs as spathic iron ore, and also mixed with clay in the form known as clay ironstone. The disulphide or iron pyrites, FeS_2 , is found in clay as nodular masses or cubical crystals of the colour of brass. Iron is found in combination in almost all rocks, the red or blue colour of many rocks being caused by the presence of ferric or ferrous oxides.

The extraction of iron from its ores. The process consists in the reduction of the oxide by means of carbon, and is carried out in a furnace with forced draught called a blast furnace. The ores contain much besides the pure iron compounds, and in order to cause these substances to be converted to fusible slags in the body of the furnace other materials must be added.

A slag is the smelter's waste material, but in the case of iron it serves to form a protecting layer on the finely divided iron as it passes down the body of the furnace. If the ore is a clay ironstone, limestone is added to form fusible aluminium calcium silicates, or if it is a calcareous ore clay may be added for the same purpose.

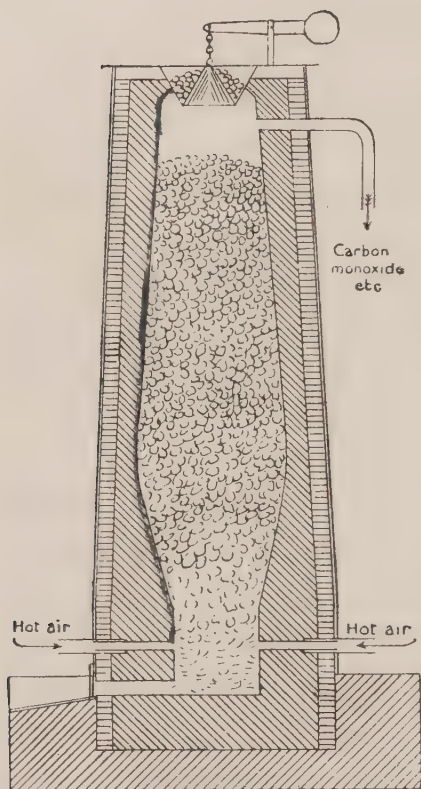


FIG. 97.

Fig. 97 is a diagram of a typical blast furnace. The furnace is first started by putting in wood and coal and igniting, and the charge of ore, coke, and other materials is poured through the opening at the top usually kept closed by means of a cup and cone arrangement. The blast of air is supplied through twyers as shown in the figure, and is heated to about 300°C . before entering the furnace by utilizing the waste gases.

Chemical changes in the furnace. Water and carbon dioxide are driven off, and the former is reduced to carbon monoxide by the glowing carbon.



Ferric oxide is reduced to iron by the carbon and to ferrous oxide by carbon monoxide; the ferrous oxide is further reduced by carbon:—



At the same time slags are formed by the action of the clay and limestone or other materials.

The finely divided iron passes down the body of the furnace in a pasty condition, and becomes covered by the melted slag which protects it from oxidation by the carbon dioxide or air.

As the iron falls lower and lower the temperature is increasing, and at the narrowest part called the boshes may be upwards of 1000°C . Eventually the iron and slag, being completely fused, fall to the lowest part and separate into two layers, the heavier iron at the bottom and the slag above.

As soon as the slag reaches a certain level it begins to flow out through an opening, and when the layer of iron reaches this level and begins to pour out, it is tapped at a considerably lower level and runs out over the damstone, and is received in sand moulds. The iron thus obtained is extremely impure, containing silicon, phosphorus, and carbon, and is called cast iron. To convert it to steel or wrought iron it is subjected to further treatment.

Wrought iron is the purest variety and most nearly approaches pure iron in its properties.

It is made by heating cast iron in an oxidizing atmosphere on a bed of iron oxide. The impurities are oxidized, and combine with this iron oxide to form slags. From time to time the lumps of pasty metal are removed and squeezed under a steam hammer, whereby the slag is pressed out. It is again heated, subjected to further hammering, and then rolled.

Conversion of cast iron to steel.

Bessemer's process. All the impurities are oxidized by forcing a blast of air through the molten cast iron; the requisite amount of carbon is added in the form of a manganese iron carbide.

Steel differs from wrought iron in containing more carbon, which may range from 0.8 to 2.5 per cent. In steel the carbon is in the form of iron carbide, in a state of solid

solution in the rest of the metal. Cast iron contains more carbon than steel; in white cast iron, formed by sudden cooling, the carbon is all in the form of carbide, whereas by slow cooling the carbon separates out partly as graphite, and grey cast iron results.

The tempering of steel. The great value of steel depends on the possibility of varying the hardness by tempering. Tempering is brought about by cooling the heated metal either suddenly or more gradually.

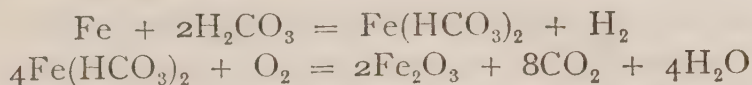
If steel heated just below redness is dipped into a bath of mercury, whereby the heat is abstracted with great rapidity, steel having the hardness of glass is produced. By regulating the temperature to which the steel is heated and the rate of cooling, all degrees of hardness can be obtained. The cause of tempering is as follows: Steel consists of a mixture of iron carbide and pure iron in varying proportions; iron carbide is hard and pure iron soft, and the solid solution of iron carbide in iron is hard.

When the solution of the carbide in iron is suddenly cooled, the hard solution remains, but when slowly cooled the carbide separates out from the iron and a mixture of the two results, which has a hardness depending on the relative proportions of pure soft iron, carbide and solution which are present.

The properties of pure iron. Iron is a grey tough metal, melting at about 1600°C. , and possesses magnetic properties to a higher degree than any other element.

It is questionable whether pure iron rusts at all in pure air free from carbon dioxide. Certainly the presence of impurities, by the formation of small voltaic circuits, hastens rusting in presence of air and water. The influence of carbon dioxide is due to the solution of the iron with formation of ferrous bicarbonate and hydrogen. In presence of oxygen this compound is decomposed, with formation of ferric oxide, carbon dioxide, and water.

The changes, put in the form of equations, are :—



Iron rust may be considered as partially hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot \text{Fe}(\text{OH})_3$.

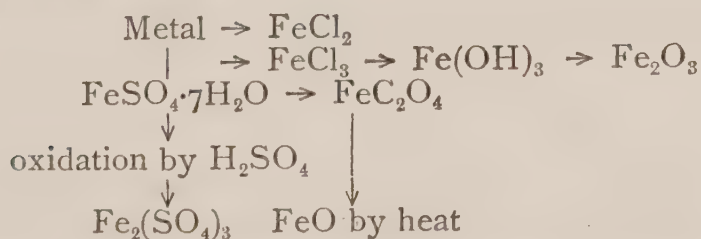
The action of iron with acids. The weakest acids attack iron, with evolution of hydrogen. Hydrochloric and sulphuric acids give the corresponding ferrous salts, hydrogen and also hydrocarbons when the iron is impure and the acid warm and not too dilute.

With dilute nitric acid, nitrous oxide (N_2O) ferrous nitrate, and water are the chief products. When very concentrated acid is used the iron becomes passive, and in this condition is not acted upon by the diluted acid.

When heated in oxygen or steam, ferroso-ferric oxide, Fe_3O_4 , is formed.

The compounds of iron. Iron can form ferrous and ferric compounds; in the former it is divalent and in the latter state trivalent.

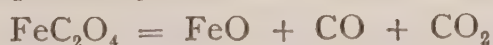
The formation of iron compounds from the metal may be illustrated thus :—



Oxides and hydroxides of iron. Besides ferric and ferrous oxides, Fe_2O_3 and FeO , a mixed oxide, Fe_3O_4 , ferroso-ferric oxide or magnetic oxide of iron is known.

Ferrous oxide, FeO , can only be obtained in a pure state when the air is rigorously excluded.

It may be prepared by (a) heating ferrous oxalate.



(b) By dehydrating ferrous hydroxide, made by the double decomposition between solutions of ferrous sulphate and sodium hydroxide, in absence of air.



Ferrous hydroxide is white, and on loss of water gives the blue-grey ferrous oxide.

Ferrous oxide is very quickly oxidized on exposure to the air, forming either the black oxide, Fe_3O_4 , or the red oxide, Fe_2O_3 .

Ferric oxide, Fe_2O_3 . This oxide is prepared from the hydroxide. Since gelatinous precipitates such as ferric hydroxide 'adsorb' salts and cannot be freed from them by washing, it is best to use ammonium hydroxide as precipitant, since ammonium salts are removable by heat.



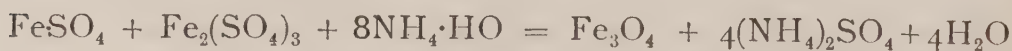
Ferric oxide may also be prepared by heating ferrous sulphate strongly.



The sulphur trioxide combines with water, forming sulphuric acid.

Ferric oxide is a dark red powder. When it has been strongly heated it is only soluble with difficulty in hydrochloric acid. It is reduced to iron by heating in hydrogen, and to FeO by carbon monoxide.

Ferroso-ferric oxide, Fe_3O_4 , is formed when iron is burned in oxygen, and also by precipitating a solution containing a ferrous and a ferric salt in molecular proportions by means of ammonium hydroxide.



It is a black magnetic powder. It dissolves in hydrochloric acid, giving a mixture of ferric and ferrous salts.

Chlorides of iron. *Ferrous chloride*, FeCl_2 , is a white volatile solid, and is prepared in the anhydrous state by

passing dry hydrochloric acid gas over heated iron. In solution it is made by dissolving iron in the dilute acid. It is very quickly oxidized in solution, especially in presence of hydrochloric acid.



Ferric chloride, FeCl_3 , is best prepared by the action of chlorine on iron (see p. 293).

It is a dark red solid, more easily volatile than the ferrous salt. Its solution in water has an acid reaction owing to hydrolysis.

Exp. 1. Oxidation of ferrous chloride and hydrolysis of ferric chloride.

A. Make a solution of ferrous chloride by the action of hydrochloric acid on iron filings placed in a small flask. Pour a little of the clear liquid into a test-tube containing a solution of sodium hydroxide. **Note** the colour of the precipitate. Shake up the contents of the test-tube with air, and **note** the change.

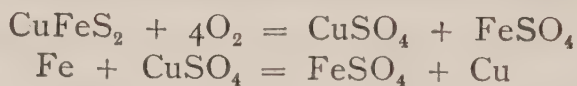
B. Fill one half of each of two test-tubes with ferric chloride solution. Heat one to boiling temperature, and **note** the difference in colour. Set aside both tubes and compare the colour of the solutions after a few days.

Hydrolysis of ferric chloride. When ferric chloride is dissolved in water, a part reacts with the water, giving a basic ferric chloride and hydrochloric acid, hence the acid reaction of the solution. The action is increased by heat, and if the solution is evaporated to dryness most of the ferric salt will be decomposed, ferric hydroxide remaining, and the hydrochloric acid escaping with the steam. The change is, however, reversible, and if the solution containing the dark red basic chloride and hydrochloric acid is allowed to stand, most of the former will react with the acid, and the solution will regain the pale yellow colour due to ferric chloride.

The action of water on a salt, whereby the oxide of the metal or a basic salt and free acid are produced, is known as *hydrolysis*. It usually takes place when the salts of weak acids or weak bases are dissolved in water.

Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (*green vitriol* or *copperas*). This is the commonest salt of iron, and the source from which the compounds of iron are usually prepared.

Preparation. Commercially it is made by allowing scrap iron to act on the liquor obtained by the action of water and air on spent pyrites. Iron pyrites generally contains a little copper, and when pyrites which has been roasted to extract the sulphur is left exposed to moist air, the copper sulphide is oxidized to copper sulphate. Iron turns out the copper and yields ferrous sulphate, which is allowed to crystallize. The copper is worked up into marketable metal.



Exp. 2. To examine the properties of ferrous sulphate.

- A.* Heat some of the powdered salt in an ignition tube. Test the liquid which collects at the mouth of the tube for sulphuric acid and water.
- B.* Fill about a quarter of each of two test-tubes with ferrous sulphate solution; to one add sodium hydroxide, and to the other add concentrated nitric acid drop by drop until the brown colour at first noticed disappears. Now add sodium hydroxide. **Note** the effect in each case.

Questions :—(i) What products were found in *A*?

(ii) Explain and write equations for the actions in *B*.

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$. This salt may be made from ferrous sulphate by evaporation of the latter with sulphuric acid. It is better to add an oxidizing agent, such as nitric acid, in addition to sulphuric acid.

Exp. 3. To make ferric sulphate from iron.

Place in a flask 50 c.c. of dilute sulphuric acid. Add half a test-tubeful of iron filings, and heat the flask gently over gauze in a draught-chamber. Continue heating until the action ceases, and filter into a basin. Now add to the filtrate 25 c.c. of dilute sulphuric acid, and drop into the liquid concentrated nitric acid until the black compound of ferrous sulphate and nitric oxide disappears, owing to complete oxidation of all ferrous to ferric iron. Evaporate the liquid to dryness on a sand bath, and examine the residue.

Put a little of the residue in a test-tube with distilled water, and note whether it dissolves. If not, leave it to stand.

Dissolve a portion of the residue in hydrochloric acid and add sodium hydroxide.

Questions:—(i) Why is it necessary to add sulphuric acid in Exp. 3?

(ii) Make out the equation for the oxidation of ferrous to ferric sulphate by nitric acid in presence of sulphuric acid. What evidence did you obtain that the action was an oxidizing one?

Tests for ferric and ferrous salts. In dilute solution ferrous salts are usually pale green, and ferric, pale yellow. They may be recognized by the action of a solution of sodium hydroxide, the dark green partly oxidized ferrous hydroxide and the red-brown ferric compound being characteristic.

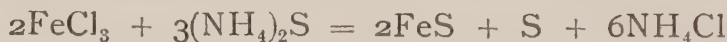
Further, the addition of potassium sulphocyanide, KCNS , to a solution of a ferric salt gives a deep blood-red coloration due to the formation of ferric sulphocyanide, $\text{Fe}(\text{CNS})_3$. The corresponding ferrous salt is colourless.

Ferrous salts give a deep blue compound, ferrous ferri-cyanide, on addition of potassium ferricyanide, $\text{K}_3\text{FeC}_6\text{N}_6$, whilst ferric salts give with potassium ferrocyanide a precipitate of Prussian blue, ferric ferrocyanide.

Ferric sulphate forms double sulphates with potassium and ammonium sulphates, which crystallize in octahedral form. They have the same crystalline form, and are isomorphous with alum (potassium aluminium sulphate) (see p. 503).

Sulphides of iron. The most important are ferrous sulphide, FeS , formed by precipitation of either a ferric or a ferrous salt with hydrogen sulphide in presence of alkali (see p. 427), and the disulphide, FeS_2 , occurring as pyrites. Ferric sulphide does not exist, and in reactions in which it might be expected to appear sulphur and ferrous sulphide are formed instead.

Thus the action of ammonium sulphide on ferric chloride takes place as follows:—



Iron pyrites is not soluble in hydrochloric or sulphuric acid, but is oxidized to a ferric salt by nitric acid. It is used largely as a source of sulphur dioxide for the manufacture of sulphuric acid. When roasted in air the following reaction takes place:—



NICKEL AND COBALT.

Neither of these metals is found free in Nature, but usually in combination with arsenic and sulphur. The processes of separation are complex, but the metals may be obtained in a coherent form by reducing the oxides with aluminium dust. They are hard, highly lustrous, magnetic metals of high melting-point. The chief alloy of nickel, *German silver*, has already been mentioned under zinc. Owing to their permanence in the air, they are used as a protective layer on other metals, such as iron.

The compounds of nickel and cobalt. The monoxides NiO and CoO are both green powders. The latter in combination with silicon oxide forms *cobalt blue* or *smalt*. Cobalt, like iron, forms an oxide, Co_3O_4 , and the basic peroxides,

Ni_2O_3 and Co_2O_3 , are known, the latter being the more stable of the two.

Salts. The salts of divalent nickel and cobalt are well known: the former are green and the latter pink in solution; when anhydrous the salts of cobalt are blue.

The common salts of these two metals are the nitrates, the chlorides, which crystallize with six molecules of water, and the sulphates, which crystallize with seven molecules and are isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The latter form double salts with the sulphates of the alkali metals of the type $\text{X}_2\text{SO}_4 \cdot \text{DSO}_4 \cdot 6\text{H}_2\text{O}$.

The sulphides NiS and CoS are both black, and are not easily dissolved by cold diluted hydrochloric acid.

Salts corresponding to the higher oxides are only known in the case of cobalt, the sulphate, $\text{Co}_2(\text{SO}_4)_3$, forming a true alum with potassium sulphate. Cobalt in this form is thus isomorphous with ferric iron.

When carbon monoxide is passed over nickel obtained by reduction of nickel oxide at a low temperature, a carbonyl, $\text{Ni}(\text{CO})_4$, is obtained as a colourless volatile liquid. Use is made of this fact for the separation of pure nickel from its ores, since neither cobalt nor any other metal behaves in a similar manner.

The relationships of iron, nickel, and cobalt. These three elements are placed together in the eighth group of the periodic system.

The elements resemble one another rather closely, all being magnetic, although iron far transcends the others in this respect; all possess high metallic lustre, are hard and have high melting-points. All three metals are isomorphous in many of their compounds, but nickel and cobalt resemble one another more closely than they do iron, their atomic weights also being very close. Iron shows a strong tendency to exist in the trivalent form, ferrous compounds being easily oxidized, cobalt shows a slight tendency, whilst nickel can hardly exist at all in trivalent form.

Practical problems. 1. Obtain a dry specimen of ferrous oxalate by precipitation from a solution of 5 g. ferrous sulphate, using a solution of oxalic acid. Heat some of the specimen in a hard tube to obtain ferrous oxide. Is it magnetic?

2. Prepare ferroso-ferric oxide from ferrous sulphate solution. Oxidize two-thirds of the latter with nitric acid, cool, and add the other third. Then add ammonium hydroxide in excess, boil, wash and dry the precipitate. Test with a magnet.

3. Obtain crystals of ferrous sulphate, starting with iron. Use a flask with a short glass exit-tube to which a piece of rubber tube closed by a bit of glass rod is attached. Make a slit in the rubber to allow the hydrogen to escape. In this way air is excluded and oxidation prevented.

4. Compare the action of ferrous sulphide and of iron pyrites when (*a*) heated in an ignition tube, (*b*) heated in a draught tube (p. 428), (*c*) treated with dilute hydrochloric acid.

5. Compare the actions of solutions of ferrous sulphate and ferric chloride on mixing with solutions of (*a*) potassium ferrocyanide, (*b*) potassium ferri-cyanide, (*c*) potassium sulpho-cyanide, (*d*) sodium hydroxide.

6. Prepare nickel sulphate and cobalt nitrate crystals, using the monoxides. Compare the actions of their solutions when treated with (*a*) sodium hydroxide, (*b*) hydrogen sulphide (alone and in presence of an alkali).

QUESTIONS ON CHAPTER XXXI.

1. Give an account of the occurrence of iron in Nature.

2. Describe and explain a method for the manufacture of cast iron.

3. How is cast iron converted into (*a*) wrought iron, (*b*) steel? What are the chief chemical differences between these three varieties of iron? How is the tempering of steel effected?

4. Describe the process of rusting, and the action of iron on steam and the common acids.

5. Starting with wrought-iron wire, how would you prepare (*a*) ferrous, (*b*) ferric, (*c*) ferroso-ferric oxides?

6. What substances are produced when (*a*) ferrous oxide, (*b*) ferric oxide, are dissolved in dilute hydrochloric acid? What remains on evaporating these solutions? How are ferrous and ferric chlorides obtained in the anhydrous state?

7. How are ferrous and ferric sulphates made, starting with iron? How are they distinguished? What is the action of heat on them?

8. Give an account of the relationships of iron, nickel, and cobalt.

CHAPTER XXXII

MANGANESE AND CHROMIUM

Manganese resembles iron, but is more easily oxidized. Like iron, it occurs chiefly in the form of one or other of the oxides, the commonest form being the peroxide, MnO_2 , called *pyrolusite*. As manganese is easily oxidized and has a very high melting-point, the only practicable means of obtaining the metal is by the use of Goldschmidt's method, i.e. the reduction of the oxide by means of aluminium powder. Prepared in this way manganese is a reddish-grey metal, extremely hard and difficult to melt. It is used for imparting great hardness to steel.

It gives the brown oxide, Mn_2O_3 , or else mangano-manganic oxide, Mn_3O_4 , when heated in air, and decomposes steam in a similar manner to iron, but more readily. The metal sets free hydrogen from most acids, even from diluted acetic acid, going into solution as a manganous salt.

Manganese oxides. The following oxides are known: MnO , Mn_2O_3 , Mn_3O_4 , MnO_2 , MnO_3 , Mn_2O_7 .

Manganous oxide, MnO , is a true basic oxide, the salts of manganese being derived from it.

Manganic oxide, Mn_2O_3 , is a basic oxide, but the manganic salts are immediately decomposed by water, with precipitation of the original oxide; double salts, such as manganese alum, $\text{K}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, are, however, quite stable in presence of water. Mn_3O_4 is a mixed oxide, like Fe_3O_4 .

Manganese dioxide, MnO_2 , is the only important oxide. It can be prepared in a pure state by precipitating manganous hydroxide in presence of an oxidizing agent, such as sodium

peroxide or calcium hypochlorite, and boiling the liquid. The black precipitate is washed by decantation with boiling water, then with dilute nitric acid, and finally with more boiling water. Thus prepared it is a black powder decomposed by strong heat into Mn_3O_4 and oxygen. With hydrochloric acid it gives manganous chloride, chlorine, and water, and on heating with strong sulphuric acid oxygen is lost and manganic sulphate is formed.

Manganese trioxide, MnO_3 , is acidic, being the anhydride of manganic acid, H_2MnO_4 , the salts of which (manganates) are well known.

The salts of divalent manganese have a characteristic pink colour.

Manganous chloride, MnCl_2 , is formed in the preparation of chlorine. The filtrate from the undissolved manganese dioxide is brownish yellow owing to the existence in solution of an unstable higher chloride, MnCl_4 , which is decomposed with loss of chlorine by boiling the liquid,



and to the presence of ferric chloride arising from impurities in the manganese dioxide.

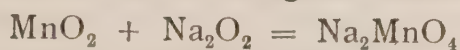
Manganese sulphate, MnSO_4 , is of a pink colour like the chloride, and is made from the latter by the action of concentrated sulphuric acid.

Manganese sulphide, MnS , is the salmon-pink coloured substance precipitated on the addition of hydrogen sulphide to an alkaline solution of a manganous salt. It is soluble in dilute acids, with formation of hydrogen sulphide and a manganous salt.

Manganic salts are only known in combination as double salts. Manganese alum, $\text{K}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is a pink compound, and is isomorphous with common alum, potassium aluminium sulphate.

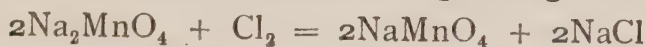
Manganates and permanganates. The trioxide, MnO_3 , possesses acidic properties. Accordingly, if an oxide of

manganese is ignited with an alkaline oxidizing agent, such as sodium peroxide or sodium carbonate and potassium nitrate, the sodium salt of manganic acid is formed.



The manganate has an intense blue-green colour, and its production is used as a test for small quantities of manganese.

By the action of oxidizing agents manganates are converted into permanganates. Thus, when chlorine is passed into a solution of a manganate, the following change takes place:—

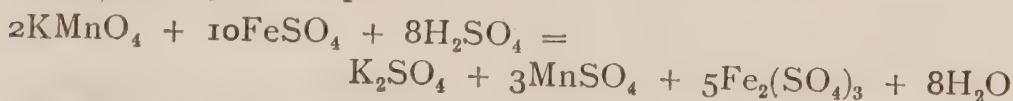


The change is brought about by the action of even so weak an acid as carbonic acid, but in this case manganese dioxide is set free. Nitric acid acts thus:—



Sodium permanganate is sold as 'Condy's fluid'. Potassium permanganate is largely used in the laboratory for the volumetric estimation of reducing substances. In acid solution two molecules give up five atoms of oxygen to the reducing substance.

Thus, in the estimation of ferrous iron, the reaction is expressed by the equation—



Detection of manganese. Manganese compounds, when fused with sodium carbonate and nitre, give a blue-green mass containing sodium manganate. When in solution manganous salts give a salmon-coloured precipitate of the sulphide on addition of ammonium chloride, ammonium hydroxide, and hydrogen sulphide.

Relationships of manganese. The compounds of manganese resemble those of iron, manganous and manganic salts being isomorphous with the corresponding compounds of iron. It is the only metallic element which finds a place in the seventh group of the periodic system, but its relation

to the halogens is only shown by the isomorphism of permanganates and perchlorates. On the other hand, manganese and sulphur are isomorphous in manganates and sulphates respectively, so that a mixture of potassium manganate and sulphate cannot be separated by crystallization.

Practical problems on manganese compounds. 1. Prepare a specimen of manganese chloride from manganese dioxide. Test for the presence of iron in the product.

2. Precipitate manganous hydroxide from a solution of manganous chloride, and examine the action of air upon it.

3. Determine whether manganous hydroxide is soluble in a solution of ammonium chloride. Devise a method of separating iron and manganese, starting with a solution containing a mixture of manganous and ferric chlorides.

4. Make a pure dry specimen of manganese dioxide, starting with manganous sulphate or chloride.

5. Examine the reaction which takes place when hydrogen is passed over strongly heated manganese dioxide.

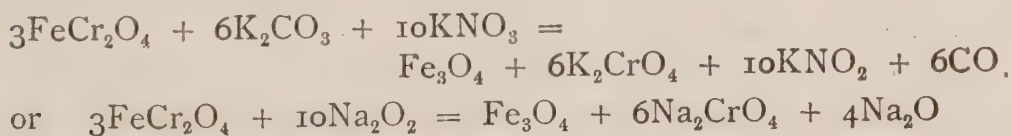
6. Make a specimen of manganous carbonate; dry it at 100°C. , and examine the effect of heating it to redness in the air. Determine whether the solid obtained is a peroxide or not.

7. Fuse manganese dioxide with sodium hydroxide and sodium nitrate in a crucible; when cold extract the mass with water, and examine the action of carbonic acid, dilute nitric acid, and chlorine on separate portions of the solution.

8. Examine the action of potassium permanganate on solutions of sulphur dioxide and of ferrous sulphate acidified with dilute sulphuric acid.

CHROMIUM.

Sources. The only important ore of chromium is chrome ironstone, FeCr_2O_4 , which may be regarded as $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. Owing to the fact that chromium forms a higher acidic oxide, CrO_3 , it follows that the salts of chromic acid, H_2CrO_4 , are formed by heating chrome ironstone with an alkali in an oxidizing atmosphere. In the laboratory this may be effected by heating chrome ironstone with potassium carbonate and nitre or with sodium peroxide.



The mass is extracted with water and decanted from the insoluble Fe_3O_4 . It is then concentrated by evaporation and acidified with sulphuric acid. Potassium sulphate and dichromate are formed and separated owing to their different solubilities.



Potassium dichromate forms the material from which all the compounds of chromium are prepared.

Metallic chromium is made by Goldschmidt's method by reduction of the green oxide, Cr_2O_3 , by aluminium dust. The melting-point is too high to make it possible to prepare it otherwise, except in the electric furnace. Thus prepared, chromium is a lustrous metal of extreme hardness, and melting at about 2000°C .

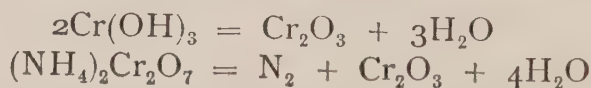
Chromium steel, an alloy of chromium and steel, is useful owing to its great hardness.

When heated in air a superficial film of oxide is formed.

Dilute hydrochloric and sulphuric acids dissolve the metal, with formation, in absence of air, of chromous salts and hydrogen, but nitric acid has no apparent action, except to render it passive (see iron, p. 523), so that after treatment with this acid the metal is not attacked by other acids.

Oxides. Several oxides are known, but only the green chromic oxide, Cr_2O_3 , and the red trioxide, CrO_3 , are important.

Chromic oxide, Cr_2O_3 . This is prepared by heating the hydroxide $\text{Cr}(\text{OH})_3$ or ammonium dichromate.



It is a dark green powder, and after being strongly heated is insoluble in acids. It is oxidized to chromate when heated with a mixture of potassium carbonate and nitrate (see oxidation of chrome ironstone).

The common salts of chromium are derived from this oxide.

Chromium trioxide, CrO_3 . When a saturated solution of potassium dichromate is treated with excess of concentrated sulphuric acid, this substance is formed as a bright crimson-coloured crystalline solid. When the liquid is cold it is filtered through an asbestos filter and washed with a little concentrated nitric acid, in which it is only slightly soluble. The nitric acid is removed by standing the mass over lime in a desiccator.

Chromium trioxide forms dichromic acid by solution in water.

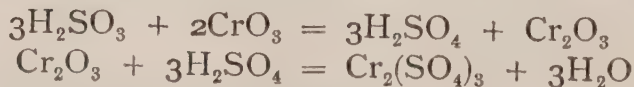


It loses oxygen when heated, and the green oxide is formed,



In solution it is a powerful oxidizing agent, and in presence of sulphuric acid is reduced, and chromium sulphate is formed.

Thus with sulphurous acid the following action takes place



In this case the sulphur of the chromium sulphate is supplied by the sulphurous acid.

Alcohol is oxidized to aldehyde, $\text{C}_2\text{H}_4\text{O}$



Salts of both divalent and trivalent chromium can exist.

Chromous salts, such as the chloride, can be formed by the action of dilute hydrochloric acid on the metal, or by reduction of chromic chloride by zinc and hydrochloric acid. In either case the air must be carefully excluded.

Chromous chloride, CrCl_2 , is a blue substance immediately oxidized to the chromic compound in air. On addition of a strong solution of sodium acetate, red chromous acetate, a fairly stable substance, is precipitated.

Chromic salts. These may be formed by solution of precipitated chromic hydroxide in the acid. When first prepared, solutions of chromic salts are green, but they become purple on standing and deposit purple crystals.

Potassium chromium sulphate, or chrome alum,



is prepared by the reduction of a solution of potassium dichromate by sulphurous acid with addition of dilute sulphuric acid.

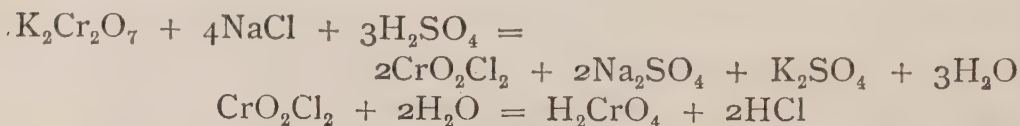


Chromic chloride, CrCl_3 . This substance can be prepared in solution from the hydroxide, and crystallizes in the hydrated form, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. On attempting to dehydrate by heat the compound loses hydrochloric acid, like the chlorides of other weak bases. In order to prepare the anhydrous compound, a mixture of pure dry charcoal and chromic oxide is subjected to the action of chlorine at a red heat; under these circumstances the volatile CrCl_3 comes off and condenses as a bright purple-coloured crystalline solid on the cooler portion of the tube.



The purple crystals are insoluble in water, but quickly go into solution with rise of temperature in presence of a trace of a chromous compound. The explanation is not forthcoming.

Chromyl chloride, CrO_2Cl_2 . When potassium dichromate mixed with sodium chloride is gently heated with concentrated sulphuric acid, chromyl chloride distils off and is obtained as a deep red liquid. It is decomposed by water, being the acid chloride of chromic acid.



* Excess of sulphuric acid must be used to prevent the reversal of the action by the water formed during the change.

Chromyl chloride is a very powerful oxidizing agent; thus when a drop is poured into alcohol ignition takes place, oxidation products of alcohol and chromic oxide, Cr_2O_3 , being formed.

Detection of chromium compounds. Chromium in any form when fused with borax forms a green bead, and the majority of its compounds are decomposed when heated in an ignition tube, with production of green chromium oxide.

Chromium sulphide is not formed in presence of water, but the blue-grey hydroxide is precipitated on addition of a soluble metallic hydroxide to a chromium salt. The hydroxide is oxidized to chromate (yellow) by boiling it with sodium hydroxide and sodium peroxide.

The solutions of soluble chromates, when made acid with acetic acid, give a precipitate of lead chromate (yellow) on addition of a soluble lead salt.

Relationships of chromium. This element is placed in the sixth group of the periodic system, parallel with the oxygen sulphur group. In certain of its chemical properties it resembles sulphur. Thus the form of many of their compounds is similar. Compare SO_3 and CrO_3 , SO_2Cl_2 and CrO_2Cl_2 , K_2SO_4 and $\text{K}_2\text{S}_2\text{O}_7$ with K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, &c.

Moreover, sulphates are isomorphous with chromates.

On the other hand, it resembles iron and manganese in its metallic compounds. Compare chromates and manganates;

the isomorphism of ferric and manganic sulphates with chromic sulphate in the alums. Ferric oxide and chromic oxide have the same crystalline form, and are isomorphous. In its tendency to play acidic functions it resembles manganese more than iron.

Practical problems on chromium compounds. 1. Prepare a specimen of pure Cr_2O_3 , using finely powdered chrome iron ore. Mix 3 grams of the ore with equal weights of nitre and potassium carbonate. Place in a large capsule and heat over a flame, with constant stirring. When the mass has melted, pour out the molten contents on to a brick. When cold, put the solid mass and the capsule into a beaker and boil until all except the iron oxide is dissolved. Decant the liquid into another vessel, and decompose the excess of potassium carbonate by dilute sulphuric acid. Reduce the dichromic acid by means of sulphur dioxide and add excess of ammonium hydroxide to the solution of chromium sulphate. Boil, filter, and wash the chromium hydroxide, dry in an oven, and finally ignite in a crucible. Make out chemical equations for all the reactions involved in the experiment.

2. Prepare a well-crystallized specimen of chrome alum by reduction of a solution of potassium dichromate acidified with sulphuric acid, using sulphur dioxide.

3. Reduce chromic chloride in solution by the action of zinc and dilute hydrochloric acid, all air having been first expelled from the apparatus by carbon dioxide. Test for a chromous salt, when the acid has all reacted with the zinc, by the addition of a strong solution of sodium acetate. A red precipitate of chromous acetate should be obtained.

4. Show the oxidizing action of chromic acid solution on alcohol in presence of dilute sulphuric acid, on concentrated hydrochloric acid, and on acidified ferrous sulphate. In the last case test for a ferric salt (*a*) with sodium hydroxide, (*b*) with potassium sulphocyanide, and (*c*) with potassium ferrocyanide.

5. Given a solution containing a ferric and a chromic salt, separate the iron as ferric oxide, leaving the chromium in solution as chromate. Add excess of sodium hydroxide to the solution, and then some sodium peroxide, and boil. Prove the absence of ferric salt in the solution, and show that it contains a chromate.

QUESTIONS ON CHAPTER XXXII.

1. What is the chief source of manganese, and how is the element extracted? What is its action with air, steam, and acids?
2. Mention the chief oxides of manganese, and explain how the pure peroxide can be made. What happens when the latter is heated (*a*) alone, (*b*) with hydrochloric acid, (*c*) with sulphuric acid?
3. How can sodium manganate be formed, starting with manganese dioxide? How is this converted into the permanganate?
4. Discuss the position of manganese in the periodic system, and point out its relationship to iron.
5. Describe how you would prepare (*a*) hydrated chromic chloride, and (*b*) the anhydrous chloride, starting with chrome iron ore.
6. What is chromyl chloride? Explain how it may be prepared, and state the action of water upon it. Compare the action of water with its action on any other acid chloride of your acquaintance.
7. Mention any chemical analogies of chromium with sulphur on the one hand and with manganese and iron on the other.
8. Why is metallic chromium difficult to prepare in a pure state? Explain how this metal may be prepared from its ore.
9. Explain how you would detect chromium in the presence of iron.

EXAMINATION PAPERS

For permission to print the following papers the authors are indebted respectively to the courtesy of (1) the Syndics of the Local Examinations of the University of Cambridge; (2) the Delegates of Local Examinations of the University of Oxford; (3) the Registrar of the University of Wales; (4) the Joint Matriculation Board of the Northern Universities; (5) the Senate of the University of London; (6) the Controller of H.M. Stationery Office.

I. CAMBRIDGE LOCAL EXAMINATIONS

Junior

EXPERIMENTAL SCIENCE II

Six questions only are to be answered.

1. Describe experiments by which you could find what takes place when a candle burns in air. In what ways does the burning of phosphorus differ from that of a candle?

2. Describe the burning of charcoal in air, and compare the effects produced when (a) a rapid current, (b) a slow current, of air is blown through a long tube packed with red-hot charcoal.

3. Give an account of the physical and chemical properties of water. Describe a method by which the quantitative composition of water can be determined.

4. How would you determine the percentage of water contained in washing-soda crystals? How could you find out the quantity of water lost by the crystals when they have effloresced in the air?

5. Give an account of the physical properties of hydrochloric and nitric acids, and compare their actions on *any two* metals.

6. A given mixture of saltpetre (nitre), sulphur, and charcoal burns very rapidly in the absence of air. How could you separate these three substances from the mixture? How could you find out the part played by each in the burning?

7. How would you determine the volume of gas given off when one gram of iron is dissolved in hydrochloric acid? By what tests would you identify the gas?

July, 1911.

EXPERIMENTAL SCIENCE III

Note. *Full details as to the observations made, together with a statement of the precautions taken to avoid error, are to be given.*

1. **Either** (a) Find the area of cross section and the volume per metre of the given wire **S** ;

or (b) Find the specific gravity of the liquid provided.

2. **Either** (a) Determine the percentage of water of crystallization in **T** ;
or (b) Examine and describe what occurs when a dilute solution of **U** is mixed with (i) caustic soda solution, (ii) dilute ammonia.

S = Copper wire 2 ins. in thickness.

T = Barium Chloride crystallized.

U = Copper Sulphate crystallized.

July, 1911.

CHEMISTRY

Only six questions may be attempted.

Candidates are advised to write equations and to give sketches of apparatus described ; elaborate drawings are not required.

1. State the law of multiple proportions. How would you verify this law in some particular case ?

2. What do you mean by the term *equivalent weight* ?

In an experiment 0.3 gram of a metal was found to liberate 85 c.c. of hydrogen at 0° C. and 760 mm. Find the equivalent weight of the metal.

(1 litre of hydrogen at 0° C. and 760 mm. weighs 0.09 gram.)

3. Describe the preparation of nitric acid. How does dilute nitric acid act upon (a) copper, (b) caustic soda, (c) calcium carbonate ?

4. How would you show by experiment that air consists of a number of different substances ? In what way could you find the percentage of one of these substances present in air ?

5. Describe an experiment to show that, when a candle burns, the matter of which it consists is not destroyed.

6. Describe one method for the preparation of chlorine, and give an account of its physical and chemical properties.

7. Give an account of the various forms of sulphur, and describe the changes which occur when sulphur is gradually heated in a test-tube to a high temperature.

8. What reactions take place when the following are heated in air : (a) chalk, (b) lead oxide (litharge), (c) lead peroxide, (d) mercury ?

July, 1911.

PRACTICAL CHEMISTRY

N.B. *Credit will be given for good observations precisely recorded, and for well-drawn inferences from them, but credit will not be given for experiments not actually made, or for conclusions without the observations on which they are based.*

Only two of the three questions are to be answered.

1. Heat **A** in a dry test-tube, and identify the volatile products.

What is the reaction of **A** towards litmus (*a*) before being heated, (*b*) after being heated?

Make a solution of **A**. Make also a solution of the substance left after heating **A**. Pour the solutions together, and describe what you observe.

2. Find which of the following solvents will dissolve **B**: water, dilute hydrochloric acid, dilute nitric acid. Describe carefully the experiments you make to find out whether the substance has dissolved or not.

3. **C** is a mixture of two substances, one of which is soluble in water and the other is not. Separate and identify them. Apply as many confirmatory tests as you can.

A = Potassium Hydrogen oxalate.

B = Lead Carbonate.

C = Sodium Chloride and Sulphur.

July, 1911.

Senior

Only six questions may be attempted.

1. Describe the preparation of (*a*) a solution of ammonia from solid ammonium chloride, (*b*) a specimen of mercuric oxide from a solution of mercuric chloride.

2. State the law of Dulong and Petit. In what cases would you apply this law to determine the probable atomic weight of an element?

A chloride of a metal contains 75.26 per cent. of metal. The specific heat of the metal is 0.057. What atomic weight would you give to the metal? (Atomic weight of chlorine = 35.5.)

3. Explain the meaning of the following: (*a*) acid-forming oxide, (*b*) basic oxide, (*c*) peroxide. Give reactions illustrating the characteristic properties of each class of oxides.

4. Describe (with equation) the preparation of chlorine from sodium chloride.

Describe three reactions showing that chlorine, in the presence of water, acts as an oxidizing agent.

5. What do you mean by *allotropy*?

How would you propose to prove that yellow and red phosphorus are varieties of the same element?

6. Give as fully as you can the reasons for assigning the formula SO_2 to sulphur dioxide.

How is sulphur dioxide converted into the trioxide? Compare the properties of the two oxides.

7. Describe the action of heat upon (a) potassium nitrate, (b) lead nitrate, (c) silver nitrate, (d) sodium hydrogen carbonate, (e) zinc carbonate, (f) calcium hydroxide.

8. Describe and explain (a) an electrolytic process for the manufacture of sodium, (b) the preparation of sodium hydroxide from sodium carbonate.

July, 1911.

PRACTICAL CHEMISTRY

N.B. *Credit will be given for good observations precisely recorded, and for well-drawn inferences from them, but credit will not be given for experiments not actually made, or for conclusions without the observations on which they are based.*

Two only of the following three questions are to be attempted. More credit will be given to Question 2 than to either of the other questions.

1. Dissolve the substance **M** in dilute sulphuric acid, and ascertain the nature of the gases evolved. Filter the solution obtained and determine the composition of the filtrate.

2. Convert about 0.5 gram of the metal **N** into its nitrate. From this prepare the oxide and determine

(a) the percentage composition of the oxide,

(b) the equivalent weight of the metal. ($\text{O} = 8$).

3. Make a qualitative analysis of **O**, which is a mixture of two simple salts.

M = Iron Filings and Iron Sulphide.

N = Copper Foil.

O = Zinc Carbonate and Ammonium Chloride.

July, 1911.

II. OXFORD LOCAL EXAMINATIONS

Junior Candidates

Draw sketches of all the apparatus you mention, and give equations when possible.

1. Describe an experiment to prepare nitrogen from the air by the use of copper. What common compounds does nitrogen form with hydrogen, and with oxygen? Show how two of them are prepared.
2. Why is it believed that (a) steam is a chemical compound of hydrogen and oxygen, (b) oxygen is an element?
3. What is Avogadro's law, and how does it help to determine the relative weights of gaseous molecules?
4. Write out the formula of a ferrous and of a ferric salt. State how it is possible to convert a ferrous into a ferric salt. What is iron pyrites and to what use is it put?
5. How is nitric acid obtained from saltpetre? Describe the apparatus used and state what is the appearance of the pure acid; what takes place when it is (a) boiled; (b) added to marble; (c) warmed with copper?
6. In what way is pure sulphur dioxide obtained? Describe an experiment by which the composition by volume of sulphur dioxide may be determined.
7. Explain why a greater yield of hydrochloric acid may be obtained from sodium chloride, than from an equal weight of potassium chloride.

July, 1911.

PRACTICAL CHEMISTRY. (A PAPER)

1. Weigh an evaporating dish of medium size, and place in it about two grams of the wire with which you are provided. Weigh the whole again. Cover the dish with a watch-glass, add dilute nitric acid, and warm gently until the whole is dissolved. (Add a drop or two of concentrated nitric acid, if solution is slow.) Then evaporate very carefully to dryness. Finally heat strongly until no further change takes place. Allow to cool and weigh again.

Calculate from the results the weight of the metal which combines with 8 parts by weight of oxygen.

Describe fully all the changes which take place during this experiment.

2. The substance marked *K* is either a chemical compound or a mixture of two chemical compounds; determine which it is by the following experiments :—

(a) Dissolve about half the substance in warm water, filter and dry any residue, and evaporate the filtrate in a basin.

(b) Describe the residues left behind upon the filter paper and on evaporation. To each residue add a little dilute hydrochloric acid, and then warm a fresh portion of each residue with caustic soda solution.

State what occurs in all your experiments. What elements are contained in the substance *K* as determined by these experiments?

July, 1911.

PRACTICAL CHEMISTRY. (*B* PAPER)

1. Determine the nature of the substances marked *G* and *W*.

Dissolve a mixture of about equal weights of *G* and *W* in dilute sulphuric acid, and gradually heat to boiling in a flask fitted with a gas delivery tube. Boil for a few minutes, and identify (a) the gas evolved during the heating, and (b) the nature of the metallic radicals in solution in the flask after the experiment.

2. Determine whether the substance *H* is an oxidizing or reducing substance; describe exactly the experiments which you perform.

July, 1911.

Senior Candidates

1. Describe a process for the extraction of oxygen from the air upon a large scale. At one time it was not believed that air played any part in combustion of bodies. When and how was this idea corrected?

2. Describe and explain the method by which the following substances may be prepared :—(a) a pure specimen of lead sulphate from red lead, (b) an approximately pure solution of hydrochloric acid from common salt.

3. You are given two gas cylinders, one of which contains a mixture of nitrogen and oxygen, and the other nitrous oxide; in what way could it be shown that one contains a mixture and the other a compound?

4. What is the action of heat upon the following bodies :—potassium nitrate, mercury, sodium bicarbonate, ammonium nitrate, manganese dioxide, lead nitrate? Give equations where possible.

5. What are the natural sources of potassium and tin?

Give an account of the preparation of—potassium carbonate, potassium chlorate, and stannous chloride.

6. Devise an experiment to show that heat is produced (a) when hydrogen and oxygen gases are mixed and exploded, (b) when ammonia and hydrochloric acid gases are mixed together.

7. What is the evidence upon which the following statements are based :— (a) the molecule of hydrogen consists of two atoms, (b) there is a simple relation between the molecular weight of any gas and its density, (c) the formula of ozone is O_3 ?

July, 1911.

PRACTICAL CHEMISTRY. (A PAPER)

1. Prepare sulphur dioxide gas from the sodium sulphite provided, and pass it for more than half an hour through a cold nearly saturated solution made by dissolving the substance *A* in water. Make a qualitative analysis of the precipitate which is thrown down. Describe its appearance and especially record the reaction of caustic potash or soda upon it in the cold, and also upon boiling.

While the gas is passing through the solution, proceed with Question 2.

2. What takes place when the substance *B* is (a) heated in a dry tube, (b) treated with dilute hydrochloric acid boiled and then allowed to cool, (c) heated with concentrated sulphuric acid?

Examine the solubility in dilute nitric, strong sulphuric and dilute acetic acids, of the residue left in the tube after strongly heating.

July, 1911.

PRACTICAL CHEMISTRY. (B PAPER)

1. The substance marked *C* may be taken as practically pure calcium carbonate. Determine the number of grams of hydrochloric acid in a litre of your bench acid, and hence determine how many grams of acid are neutralized by each gram of the substance marked *D*, using methyl orange as the indicator. (The bench acid should be diluted before use.)

2. Describe fully the effect of heat upon the substance marked *E*, noting whether any gas or gases are evolved, and how the residue reacts with dilute hydrochloric acid.

July, 1911.

III. UNIVERSITY OF WALES

Matriculation

Six questions only are to be attempted.

1. How would you prepare a specimen of slaked lime in the laboratory from a small piece of chalk? How does slaked lime differ in its properties from chalk? What common substances when allowed to act upon slaked lime suspended in water will produce a clear solution? Give equations representing each of the actions to which you refer.

2. How may small pieces of the common metals iron, magnesium, mercury and tin be oxidized most conveniently? Describe the appearance and properties of each of these metals and of its oxide.

3. Describe the two crystalline forms in which sulphur is known and state how a specimen of each might be obtained from a quantity of powdered sulphur. Under what conditions are they respectively stable? How may sulphur be made to combine with (a) iron or copper, (b) hydrogen, (c) carbon?

4. What is the effect (a) of passing a current of hydrogen over red hot iron oxide, (b) of passing a current of steam over red hot iron? Draw the apparatus which would be used for carrying out these experiments and give an explanation of the reactions which take place.

5. State exactly how you would proceed, if you were required to find the volume of hydrogen evolved by one gram of zinc when it is placed in dilute sulphuric acid. Draw the apparatus you would use and state what precautions you would take to ensure an exact result.

6. What is an empirical formula? Give the names and empirical formulae of some of the simpler compounds of carbon with hydrogen and state how you would prepare any one of them.

Calculate the empirical formula of a substance of the following percentage composition.

C = 40.67. O = 27.12. H = 8.47. N = 23.73.

7. Describe any experiments you have made to find out what changes are brought about in the composition of air when an animal breathes. What are the chief differences between ordinary and expired air?

C = 12. O = 16. H = 1. N = 14.

Sept., 1910.

Six questions only are to be attempted.

1. How would you prepare and collect a quantity of oxygen and how would you convert it into its more active form? Describe the properties of each of these forms.

2. What is a hard water? State and explain what is seen when a current of carbon dioxide is passed into lime water until no further action takes place and the liquid is subsequently heated. How will the hardness of the water vary while these operations are being carried out?

3. How would you prepare and collect a quantity of (a) nitrous oxide, (b) nitric oxide, and how would you show that any given volume of the former contains twice as much nitrogen as the same volume of the latter?

4. Describe two different methods of obtaining carbon dioxide from marble. Which method would you employ in the laboratory and why? What volume of carbon dioxide measured at 15°C . and 756 mm. pressure could be obtained from 10 grams of marble?

5. State briefly how the compounds which sulphur forms with (a) oxygen, (b) hydrogen, (c) carbon are prepared, and give their chief properties.

6. What is seen when a small piece of sodium is thrown upon water? How are the substances which are produced commonly prepared? If two grams of sodium were used what weight of sulphuric acid would be required to neutralize the resulting liquid?

7. What experiments would you make to ascertain (a) whether a quantity of ammonia is mixed with nitrogen, (b) whether a quantity of nitrogen is mixed with ammonia, (c) whether a quantity of hydrogen chloride is mixed with hydrogen, (d) whether a quantity of hydrogen is mixed with hydrogen chloride?

8. Write a short essay on the atomic theory.

$\text{H} = 1. \quad \text{C} = 12. \quad \text{Ca} = 40. \quad \text{Na} = 23. \quad \text{O} = 16. \quad \text{S} = 32.$

One litre of hydrogen measured at 0° and 760 mm. pressure weighs 0.09 gram.

June, 1911.

IV. JOINT MATRICULATION EXAMINATION OF THE UNIVERSITIES OF MANCHESTER, LIVERPOOL, LEEDS, AND SHEFFIELD

Give equations where possible.

1. What are the principal characteristics of acids and bases? Describe carefully how you would prepare a specimen of a pure crystalline salt from (a) zinc; (b) caustic potash; (c) lead oxide; (d) copper carbonate. Give equations.
2. Calculate the density, taking hydrogen at N.T.P. as unity, of a mixture of 2 litres of ammonia and 1 litre of hydrogen at 0°C . and 760 mm. How could you obtain each gas in a pure condition from the mixture?
3. Describe any method by which oxygen can be obtained from air. What is produced by the combustion of the following substances in oxygen: (a) sulphuretted hydrogen; (b) iron; (c) marsh gas?
4. How may nitric acid be prepared in the laboratory? Describe carefully what happens when nitric acid is brought into contact with limestone and copper filings respectively. State how you would collect the gaseous product in each case.
5. Suggest, with sketches of apparatus, experiments by which you could show that hydrogen chloride contains hydrogen and chlorine. What weight of sodium chloride could be theoretically obtained from 1 litre of hydrochloric acid gas, measured at N.T.P.? [$\text{Cl} = 35.5$; $\text{Na} = 23$.]
6. Describe how you would show, and explain, the effect of heating the following substances in air: (a) copper nitrate; (b) zinc carbonate; (c) sodium bicarbonate; (d) lead.
7. How would you prove the identity of the liquid produced by passing hydrogen over heated copper oxide with pure water? Point out the differences between hard water, soft water, and sea water.

Sept., 1910.

Candidates are required to show by their answers that they have seen experiments illustrative of the subjects included in the syllabus, and that they have themselves performed a variety of simple qualitative and quantitative experiments.

Give equations where possible.

1. How may pure oxygen and chlorine be obtained from potassium chlorate? Give sketches of the apparatus you would employ in each case.

2. What is the action of cold water upon the following substances: (a) sulphur dioxide; (b) sulphur trioxide; (c) nitrogen peroxide? What salts are formed on treating the resulting solution in each case with sodium hydroxide?

3. Explain how you would obtain hydrogen from steam and sulphuretted hydrogen respectively.

4. What do you understand by the terms 'oxidizing agent' and 'reducing agent'? Classify the following, with examples of their use, as oxidizing or reducing agents: chlorine, sulphur dioxide, carbon, ozone.

5. How would you obtain carbon dioxide and carbon monoxide from a mixture of these gases? One litre of such a mixture on passing through a long tube containing red-hot carbon gave 1,600 c.c. carbon monoxide measured under the same conditions. Calculate the composition by volume of the mixture.

6. Describe briefly the chemical changes which occur when concentrated sulphuric acid acts upon (a) copper; (b) common salt; (c) potassium iodide.

7. How could you show that hydrogen chloride contains half its volume of hydrogen measured at the same temperature and pressure? Calculate the weight of ammonium chloride produced by passing 10 litres of hydrogen chloride at N.T.P. into an aqueous solution of ammonia.

(N = 14; C = 35.5; 1 litre of hydrogen at N.T.P. weighs 0.09 gram.)

July, 1911.

V. UNIVERSITY OF LONDON

Matriculation

Six questions only are to be attempted.

1. Describe, with a sketch of the apparatus, how you would prepare a solution of hydrochloric acid. Given a supply of Iceland spar (CaCO_3) suggest a method by which you could employ this substance to find the percentage by weight of hydrogen chloride in your solution.

2. From what sources is sulphur obtained? Give an account of any *three* experiments you have performed, or seen performed, illustrating the properties of sulphur. How would you attempt to find whether the solid substances formed by passing (a) sulphur vapour, (b) hydrogen sulphide, over red-hot iron filings are the same?

3. Describe carefully how you would prepare from iron wire specimens of (a) ferric oxide (Fe_2O_3), (b) crystalline ferrous sulphate. What weight of iron wire would you use to obtain 20 grams of ferrous sulphate crystals ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)?

4. What do you understand by the basicity of an acid? Illustrate your answer by reference to actual examples. If you were given some sodium carbonate and sulphuric acid, how would you prepare a specimen of crystallized sodium hydrogen sulphate?

5. How would you ascertain whether a sample of water had dissolved any air and, if so, how would you measure approximately the volume of it contained in one litre of the water? Given a 500 c.c. stoppered flask containing 'recovered air', describe, in detail, how you would find out whether it differed in composition from ordinary air?

6. Calculate the weight of one litre of a mixture of two volumes of nitrogen and one volume of oxygen, measured at 0°C . and 76 cms. pressure, and compare it with the weight of one litre of nitrous oxide, measured under the same conditions.

Nitric oxide, nitrous oxide, and nitrogen peroxide respectively are (a) shaken with water, (b) mixed with an equal volume of oxygen and shaken with water. What changes would you expect to observe in these experiments?

7. Describe two ways of preparing an oxide from lead and one method of regaining the metal from the oxide. What is the action of nitric acid on (a) litharge, (b) red lead?

8. How would you prove experimentally that the weight of the product obtained when sulphur is burned in oxygen is greater than that of the sulphur which has disappeared? Draw a diagram of the apparatus you would use. How may the gaseous product be regained after this experiment? How would you identify it?

[H = 1; C = 12; Ca = 40; Cl = 35.5; Fe = 56; N = 14; O = 16; S = 32. 1 litre of hydrogen, measured at 0°C . and 76 cms. pressure, weighs 0.09 gram.]

Jan., 1911.

Six questions only are to be attempted.

1. A quantity of air is drawn very slowly by means of an aspirator through a long glass tube which is packed with charcoal and heated to redness. Describe the chemical changes which occur in the tube. What would be the approximate composition of the gas which collects in the aspirator? What modifications would you make in carrying out this experiment in order to use it to obtain a specimen of nitrogen from the atmosphere?

2. State the law of multiple proportions, and suggest some simple experiment by which the law might be illustrated in the laboratory.

A certain salt forms two crystalline compounds which have the following percentage composition:—

(a) Anhydrous salt 63.86.

Water 36.14.

100.00

(b) Anhydrous salt 89.83.

Water 10.17.

100.00

Show how these numbers illustrate the law.

3. Describe, with sketches of the apparatus, how you would prepare and collect specimens of each of the oxides of sulphur. What occurs when these oxides are respectively brought in contact with an aqueous solution of sodium hydroxide?

4. Explain what you understand by (a) chemical change, (b) physical change. Illustrate your answer by describing experiments which can be made with phosphorus. Describe how you would prepare a crystalline specimen of sodium phosphate from phosphorus.

5. How would you prepare and collect several jars of *dry* ammonia? Explain what you would see if a lighted taper were held near the mouth of one of the jars containing the gas.

What would be the weight of the solid product obtained if 200 c.c. of ammonia, measured at 17° C. and 75 cm. pressure, were mixed with an equal volume of hydrogen chloride measured at the same temperature and pressure?

6. How is sodium bicarbonate related to sodium carbonate? How would you prepare specimens of these salts from sodium hydroxide? Give some account of their properties and explain for what purposes they are used.

7. Describe two different experiments which show that chlorine has a strong tendency to unite with hydrogen. How would you obtain specimens of the two chlorides of iron? How may the chlorine which these compounds contain be set free?

8. What do you understand by the terms—basic oxide, anhydride, peroxide, acid? Give examples. Given a supply of both sodium chloride and copper nitrate how would you prepare specimens of two acids and one base?

[H = 1; N = 14; Cl = 35.5. 1 litre of hydrogen, measured at 0° C. and 76 cm. pressure, weighs 0.09 gram.]

June, 1911.

VI. ARMY ENTRANCE EXAMINATION

CHEMISTRY QUESTIONS

1. How would you prepare a sample of pure oxygen from atmospheric air? What experiments would you perform to prove its purity? Sketch any apparatus you would use.

2. When magnesium wire is dissolved in dilute sulphuric acid hydrogen is evolved. Describe the apparatus you would require, and the method you would adopt, to ascertain the relation between the weight of magnesium dissolved and the volume of the gas liberated. What other data would you require to determine the equivalent weight of the metal?

3. Describe a method of preparing pure chlorine. Describe two experiments to illustrate the great affinity of chlorine for hydrogen. Compare the bleaching action of chlorine with that of sulphur dioxide.

4. 20 c.c. of a solution of sulphuric acid, containing 24.5 grams of pure acid per litre, are required to neutralize 50 c.c. of a solution of caustic soda. 25 c.c. of this soda solution will just neutralize 50 c.c. of a solution of nitric acid. Calculate the amount of pure nitric acid in a litre of the latter solution.

[at. wts. $H = 1$, $S = 32$, $N = 14$, and $O = 16$.]

5. Explain what happens when the following substances are heated in the air, describing clearly any changes in weight, appearance and properties:—zinc oxide, copper nitrate, ferrous sulphate, tin.

6. Describe carefully how you would determine the percentage of water of crystallization in a sample of washing soda.

How would you prepare from washing soda a specimen of sodium bicarbonate?

7. A quantity of oxygen at $15^{\circ}C$. and 75 cm. pressure has been collected over water and is found to occupy a litre. Find the volume of dry oxygen as measured at $0^{\circ}C$. and 76 cm. pressure, being given that the maximum pressure of aqueous vapour at $15^{\circ}C$. is 12.7 mm.

8. What do you understand by 'reduction'? What reducing agents would you use (a) in preparing crystalline ferrous sulphate from ferric sulphate, (b) in preparing copper from copper oxide, (c) lead from lead oxide? Give your reasons.

9. From what sources are nitric acid and the nitrates obtained? Describe an experiment to show that nitric acid is an oxidizing agent. How would you obtain from nitric acid a specimen of oxygen?

10. How may litharge and red lead be produced? What happens when these substances are (a) heated, (b) treated with nitric acid, (c) warmed with strong hydrochloric acid?

11. Carbon monoxide is a stable gas which can be made to combine directly with oxygen and with chlorine. The question arises:—Is it an element or non-element? What experiments would you make to decide this point?

June, 1911.

LABORATORY WORK.

Two of the following questions were set in each batch.

1. Find, by evaporation, the weight of salt contained in each 50 c.cm. of the solution 'A'.
2. The substance 'B' is an oxide, and you are required to ascertain if it is basic, acidic, or neutral. Prepare from it a well-crystallized specimen of a salt.
3. The substance 'C' is an intimate mixture of barium carbonate and potassium chlorate. Determine the percentage of barium carbonate in the mixture.
4. From the metal 'D' prepare a well-crystallized specimen of its nitrate.
5. Determine the percentage of non-volatile impurity in the sulphur marked 'E', by heating a convenient quantity in a porcelain crucible till no further loss in weight is observed. Ascertain if the residue is soluble in water.
6. The substance 'F' is the carbonate of a metal. Prepare from it a well-crystallized specimen of the sulphate of the metal.
7. Identify the gases evolved on heating the salt 'G', and determine the percentage of residual matter when the heating is continued till no further change occurs.
8. Carefully examine and fully describe the action of the common acids and of potassium hydroxide on the metal 'H'.
9. Find if the salt 'I' contains water of crystallization, and if it does, determine the weight of water in 100 grams.
10. Prepare a specimen of the oxide of the metal 'J'.
11. Find which of the two solutions of nitric acid 'K' and 'L' is the weaker. Assuming that the weaker solution contains 6.3 grams of HNO_3 per litre, state the weight of nitric acid in each litre of the stronger solution.
12. Identify the liquid evolved on strongly heating the salt 'M'.
13. The salt 'N' evolves water when it is heated. Ascertain if this loss is due to water of crystallization in the salt; also find the total percentage loss in weight which occurs when the salt is heated till no further change takes place.
14. Prepare a specimen of the oxide of the metal 'O'. The specimen should weigh at least one gram.
15. You are provided with two solutions 'P' and 'Q', and you are required to ascertain the nature of these as far as is possible by pouring small quantities of each solution over metals and into acids. Find also the volume of 'P' which will exactly neutralize 50 c.cm. of 'Q'.
16. The substance 'R' is a carbonate of a metal. Prepare from it a well-crystallized specimen of the nitrate of the metal.

17. Ascertain if the substance 'S' changes when it is heated in air, and if it does, determine the percentage gain or loss in weight incurred.
18. Fully report on the action of the common acids and common alkalies on the salt 'T'.
19. Measure the volume of gas evolved on dissolving 1 gram of the substance 'U' in dilute hydrochloric acid.
20. From the metal provided and marked 'V' prepare a specimen of oxide. The specimen should weigh at least one gram.
21. Find the percentage increase in weight which the metal 'W' undergoes when heated in air. You are advised to heat the metal cautiously in a covered crucible, removing the lid from time to time.
22. Study the action of the common acids on the metals 'X' and 'Y', and from your observations state what each metal probably is.

A = Potassium chlorate.

B = Magnesium oxide.

D = Lead foil.

F = Zinc carbonate.

G = Ammonium chromate.

H = Aluminium foil.

I = Magnesium sulphate.

J = Magnesium wire.

M = Hydrogen sodium sulphate.

N = Magnesium carbonate.

O = Tin.

P = Sodium carbonate.

Q = Nitric acid.

R = Lead carbonate.

S = Magnesium carbonate.

T = Ammonium chloride.

U = Zinc foil.

V = Zinc.

W = Magnesium turnings.

X = Zinc foil.

Y = Lead foil.

APPENDIX

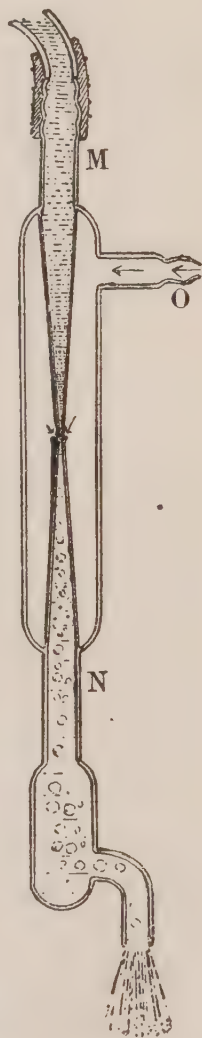
P. 120, Exp. 2. It is important to have all the connexions quite air-tight, especially the cork at the top of the lamp-glass. Neglect of this is one of the chief causes of failure.

The lamp-glass with holes near the base is such as is commonly used with erect incandescent gas-burners.

A gentle current of air usually works better than a rapid one.

A considerable quantity of liquid may be collected by using a Clarke's Pyramid Night-light, after replacing the wick with a bit of ordinary wax taper (Bryant & May's 'Mid' tapers).

The Bunsen water-pump is illustrated in the diagram. A stream of water, under great pressure, passes down the central tube *M*, and escapes through a narrow orifice into a second tube *N*. The rapid flow of water draws air into the opening between the upper and lower tubes, in the direction indicated by the arrows. If the water pressure is sufficient, nearly a complete vacuum may be produced in a flask attached at *o*. With a slow current of water, the pump may be used for any experiments in which it is necessary to draw gases through tubes, &c.



P. 226. *Eudiometer*. This type of eudiometer is made by Müller & Orme, 148 High Holborn, W.C.

P. 340. *Copper-sulphate pumice*, for absorbing vapour of hydrochloric acid, is made by heating granulated pumice-stone (separated from the powder by sifting) with a fairly strong solution of copper sulphate. The liquid is poured off and the solid residue heated to 200°C . in an air-oven until the blue colour disappears.

P. 438. *Exp. 7. Platinized asbestos* is made by dipping previously dried asbestos into a fairly strong solution of platinum chloride and then into one of ammonium chloride. A deposit of the double chloride of platinum and ammonium is formed on the asbestos; on drying and igniting the double chloride decomposes, leaving finely divided platinum.

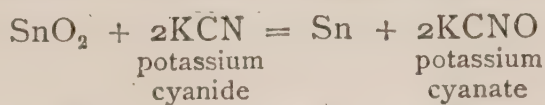
BLOWPIPE TESTS FOR METALS.

In the laboratory, reduction of salts to their metals on the small scale can be effected by means of the reducing blowpipe flame. The general method is (1) to try the reducing flame alone (see p. 326). If no metallic bead is obtained, (2) mix the substance in a mortar with about three times its bulk of dehydrated sodium carbonate, place a *little* in a shallow hole in the charcoal, and direct the reducing flame on to it. The sodium carbonate melts and enters into double decomposition with the compound, yielding the carbonate. This breaks up into the oxides of the metal and carbon. The flame then reduces the oxide.

Note the colour of the bead; the colour of the incrustation of metallic oxide (if any) which forms on the charcoal round the hole. Find whether the bead is malleable or brittle.

If no bead is obtained, (3) mix about equal bulks of the substance, sodium carbonate, and potassium cyanide (*very poisonous*) in a mortar and try again.

The cyanide is a direct reducing agent, and is necessary for tin compounds and often for copper compounds.



Identify the metals in the substances given by reference to the following table :—

Name of metal.	Nature of metallic bead.	Colour of incrustation.
Lead	White ; malleable	Yellow (PbO)
Bismuth	White ; brittle	Yellow (Bi ₂ O ₃)
Antimony	White ; brittle	White (Sb ₂ O ₃)
Zinc	None	White ; yellow when hot (ZnO)
Arsenic	None	White ; smell of garlic
Cadmium	None	Brown (CdO)
Copper	Red ; malleable but hard	None
Tin	White ; malleable	None or white (SnO ₂)
Iron	No bead, but black magnetic powder	None

PRESSURE OF AQUEOUS VAPOUR IN MILLIMETRES OF MERCURY

t° C.	mm.	t° C.	mm.	t° C.	mm.
0	4.60	11	9.79	22	19.66
1	4.94	12	10.46	23	20.89
2	5.30	13	11.16	24	22.18
3	5.69	14	11.91	25	23.55
4	6.10	15	12.70	26	24.99
5	6.53	16	13.54	27	26.51
6	7.00	17	14.42	28	28.10
7	7.49	18	15.36	29	29.78
8	8.02	19	16.35	30	31.55
9	8.57	20	17.39		
10	9.17	21	18.50		

1 litre of hydrogen at S.T.P. weighs 0.0899 g.

„ „ air „ „ „ 1.293 g.

SYMBOLS AND ATOMIC WEIGHTS OF THE COMMON ELEMENTS

Aluminium	Al	27	Manganese	Mn	55
Antimony	Sb	120	Mercury	Hg	200
Argon	A	40	Neon	Ne	20
Arsenic	As	75	Nickel	Ni	58.7
Barium	Ba	137.5	Nitrogen	N	14
Bismuth	Bi	208	Oxygen	O	16
Boron	B	11	Phosphorus	P	31
Bromine	Br	80	Platinum	Pt	195
Caesium	Cs	133	Potassium	K	39
Calcium	Ca	40	Radium	Ra	226.4
Carbon	C	12	Rubidium	Rb	85.5
Chlorine	Cl	35.5	Selenium	Se	79.2
Chromium	Cr	52	Silicon	Si	28
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63.5	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	88
Gold	Au	196.7	Sulphur	S	32
Helium	He	4	Tantalum	Ta	181
Hydrogen	H	1	Tellurium	Te	127.5
Iodine	I	127	Thallium	Tl	204.0
Iron	Fe	56	Tin	Sn	118
Krypton	Kr	83	Tungsten	W	184
Lead	Pb	206.4	Uranium	U	238.5
Lithium	Li	7	Xenon	Xe	130
Magnesium	Mg	24	Zinc	Zn	65

The figures given are for use in calculations and are only approximate in some cases.

ANSWERS TO NUMERICAL QUESTIONS

Questions on Chap. III, page 43.

9. 34.7. 11. (a) 73.5. (b) 14°C.
 13. 39.8 g. 14. At 19°C. 1.14; at 30°C. 1.43.
 15. 38.6 g. of salt; 1.4 g. of lead chloride.

Questions on Chap. IV, page 58.

9. 36.3 per cent.

Examples V (a), page 64.

1. 288° A.; 258° A.; 273° A.; 546° A.; 0° A. 2. 110.14 c.c.
 3. 3052.08 cu. m. 4. 0.929 l. 5. -49° 5 C.
 6. At 0° C. $\frac{\text{vol. of } X}{\text{vol. of } Y} = \frac{5}{12}$.
 7. The vol. of coal-gas is greater by 442.4 c.c. (approx.).
 8. -45.5° C. 9. Vol. of air is 4.4 c.c. greater.

Examples V (b), page 67.

1. (a) 97.4 c.c. (b) 102.7 c.c. 2. 18.75 cm. of mercury.
 3. $\frac{29}{38}$ litre. 4. 6.857 litres.
 5. (a) 17.5 cub. ft. (b) 13.125 cub. ft.
 6. 684 mm. 7. 0.0257 l. 9. 2.4.
 10. (a) 550 mm. of mercury. (b) 132 c.c.
 11. (a) 735.3 mm. (b) 176.47 c.c.

Examples V (c), page 69.

1. 78.44 c.c. 2. 15.95 l. 3. 16.77 l. (approx.).
 4. 76.91 cub. in. 5. 31.21 inches.
 6. Increase of 2.74 lb. per sq. in.
 7. (a) 15.7 c.c. (b) 17.1 c.c.

Examples V (d), page 74.

1. 605 mm.; 39.8 c.c. 2. 743.9 mm. 3. 592.3 mm.; 38.96 c.c.
 4. 102.3 c.c. 5. 17.2 g. 6. 1.223 g.
 7. 79.938 Km. 8. Reduced to 561 mm.

Questions on Chap. VIII, page 117.

3. From mercury oxide . 7.4 % of oxygen.
 „ nitre . . . 15.84 % „ „
 „ potassium chlorate . 39.18 % „ „
 9. 1 c.c. weighs (a) 0.00165 g. (b) 0.00157 g. (approx.).

Questions on Chap. XIII, page 231.

7. $\frac{1}{8}$ that of hydrogen. 8. 1.517.
 24. 33.2 % oxygen, 66.8 % hydrogen.
 25. 88.8 % oxygen, 11.1 % hydrogen.

Questions in Chap. XIV.

(The weight of 1 l. of hydrogen at S.T.P. is taken as 0.09 g.)

Page 257. (a) 2250 c.c. (b) 250 c.c. (c) 6050 c.c.

Page 260. 6. 31.78 7. 30.03.

8. (a) 1.53. (b) 12.24.

21. (a) 100 c.c. (b) 200 c.c.

Questions XV a, page 272.

2. 64; 32 g. of each; SO_2 . 3. 13.88; 27.76; N_2 . 4. 28.
 6. The equivalents are 18.66 and 20.96 respectively.

Questions XV b, page 274.

1. (a) 205.7. (b) 200.5. (c) 59.2. (d) 122.3.

2. 5.48, 16.6, 11.2, 12.2 calories respectively. 3. 0.4.

4. 58.9; ii; 117.8. 5. 42; 210; v.

7. E.W. 37.6; A.W. 112.8. 8. A. 56. B. 112.

Questions XV c, page 282.

11. Simplest, CO_2 ; true, CO_2 . 12. CO ; C_3O_3 .

13. CH_4O . 14. CH_2 . 15. C_2H_2 ; C_6H_6 . 16. Pb_3O_4 .

17. 32.5. 19. 8.94; iii; 26.8; XCl_3 .

20. (a) 56. (b) 136. (c) 92. (d) 286. (e) 46. (f) 948.

21. (a) Calcium 71.4. (b) Carbon 88.2. (c) Carbon 39.1.

Oxygen 28.5. Hydrogen 11.7. Hydrogen 8.7.

Oxygen 52.1.

(d) Sodium 16.08. (e) Carbon 52.1. (f) Aluminium 5.6.

Carbon 4.19. Hydrogen 13.0. Sulphur 13.5.

Oxygen 16.77. Oxygen 34.7. Oxygen 26.9.

Water 62.93. Potassium 8.2.

Water 45.6.

22. (a) CH . (b) Fe_2O_3 . (c) KNO_2 . (d) $\text{ZnSO}_4 + 7\text{H}_2\text{O}$.

25. (a) 247.7 g. (b) 0.41 g. (c) 164.3 g. of zinc sulphate; 2.04 g. of hydrogen.

26. (a) 67.2 l. (b) 28.2 l. (c) 63.3 l.

27. (a) 167.2 g. (b) 5.98 l.

28. (a) 22.4 l. (b) 21.79 l. (c) 22.02 l.

Questions on Chap. XVI, page 313.

17. (a) 160.3 g., (b) 52.2 g., (c) 47.8 g., approx.
 18. (a) 72.9 g., (b) 23 l., (c) 24.6 l., approx.
 19. (a) 10 l. (b) 10.76 l.
 20. (a) 20 l. (b) 28 l.

Questions on Chap. XVIII, page 364.

4. 27.27 % carbon ; 72.72 % oxygen.
 12. 35.2 l. (approx.) ; 438 g. of acid solution.
 13. (a) 44.6 g., (b) 40.9 g., approx.
 14. (a) 7.85 g. (b) 4 l.
 29. C_2H_4 .
 32. 25 l.

Questions on Chap. XX, page 407.

3. Quicklime, 1046.64 g. ; slaked lime, 1383.06 g. ; caustic potash, 2093.28 g. ; caustic soda, 1495.2 g.
 10. 9.39 l. nitrogen ; 22.64 c.c. water ; 78.87 g. copper.
 17. 62.37 g.
 19. (a) 42 l. (b) 44.97 l.
 20. (a) 71.52 g. (b) 66.71 g.
 29. (a) 0.6237 ton. (b) 0.7413 ton.
 31. (a) 4.58 l. (b) 4.2 l.
 33. Nitrous oxide, 63.64 % of nitrogen, 36.36 % oxygen.
 Nitric oxide, 46.66 " " 53.33 "
 Nitrogen trioxide, 36.84 " " 63.15 "
 Nitrogen peroxide, 30.43 " " 69.56 "
 Nitrogen pentoxide, 25.92 " " 74.07 "
 34. Nitrous oxide, 10 l. nitrogen, 5 l. oxygen.
 Nitric oxide, 5 l. " 5 l. "
 Nitrogen peroxide, 5 l. " 10 l. "

Questions on Chap. XXII, page 445.

6. 70 l.
 8. 82.95 g. of acid ; 25.45 l. of gas.
 13. 48.59 g. of copper ; 18.57 l. of gas.
 15. 38.06 l.
 16. 27.32 g.

564. ANSWERS TO .NUMERICAL QUESTIONS

21. (a) Sodium 36.57.
Sulphur 25.39.
Oxygen 38.09.

(c) Iron 63.64.
Sulphur 36.36.

31. 294.7 l. CO_2 .
589.5 l. SO_2 .
29,355.8 l. O_2 .
113,760 l. N_2 .

(b) Sodium 22.11.
Hydrogen 0.96.
Sulphur 30.77.
Oxygen 46.16.

(d) Iron 46.66.
Sulphur 53.33.

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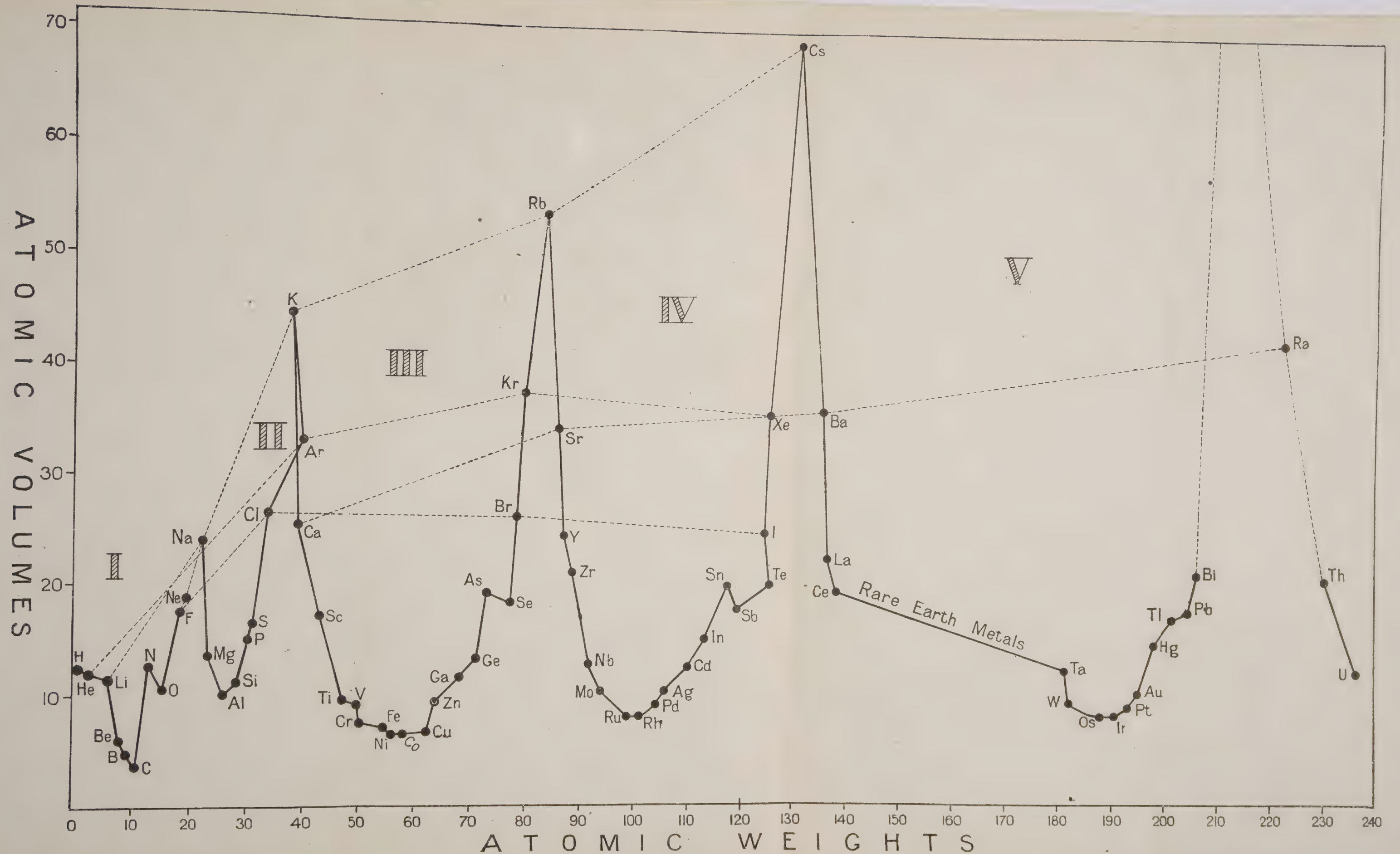
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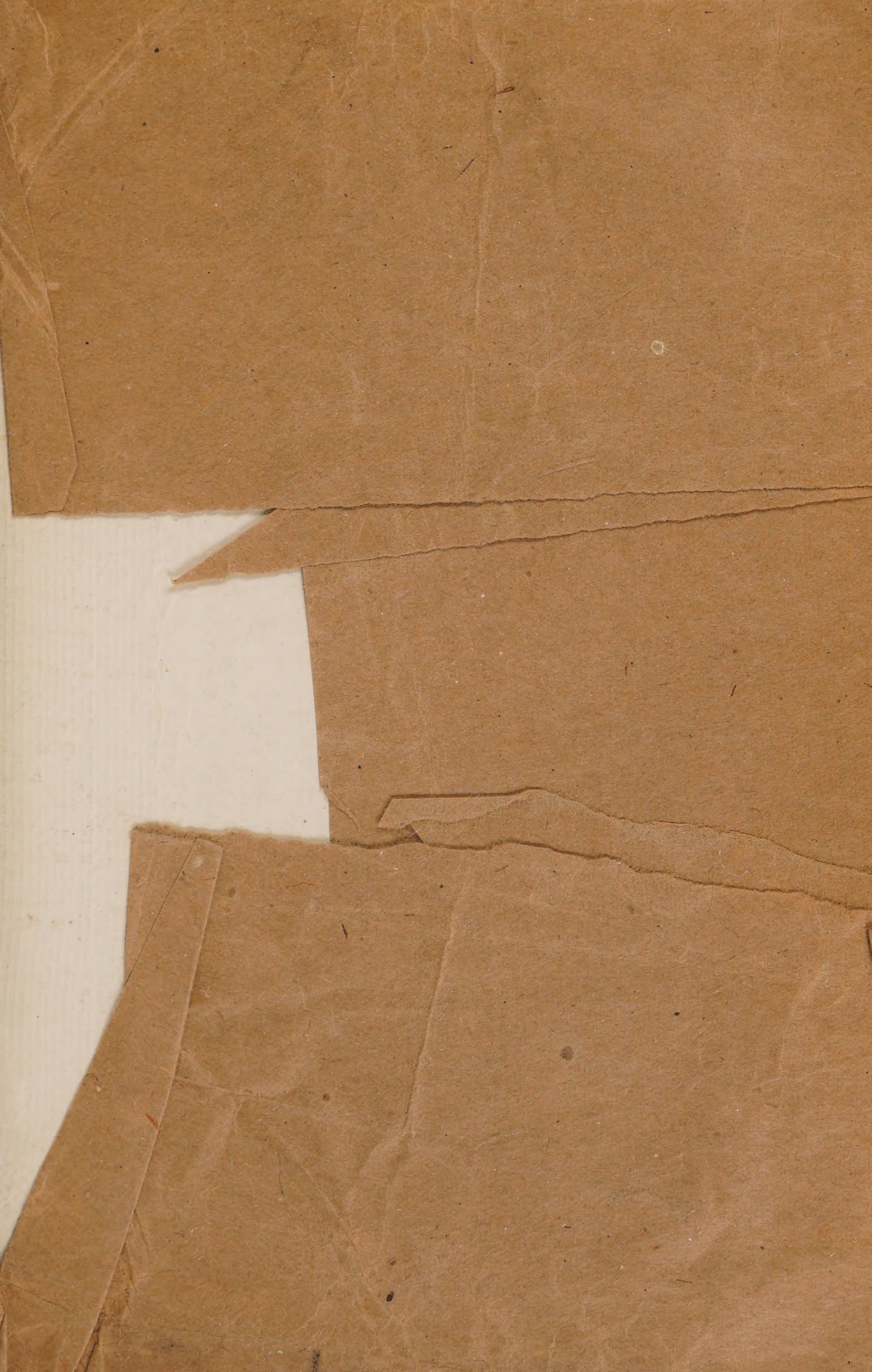
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Some of the Groups of Elements are linked up by dotted lines Roman numerals represent the periods, I and II being short, & the rest long periods.



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